ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF PMMA-*b*-PS CONTAINING A CROWN ETHER UNIT AT FOCAL POINT VIA COMBINATION OF ATRP AND NMP ROUTES

M.Sc. Thesis by

Özcan ALTINTAŞ

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

JANUARY 2006

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(515041025)

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Supervisor (Chairman) : Prof. Dr. Ümit TUNCA (İ.T.Ü)

Members of the Examining Committee : Assoc. Prof. İsmail YILMAZ (İ.T.Ü.)

Assoc. Prof. Nergis ARSU (Y.T.Ü.)

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ATRP VE NMP YÖNTEMLERİ İLE CROWN ETER BAĞLANTI NOKTASI İÇEREN KOPOLİMERLERİN SENTEZİ

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Özcan ALTINTAŞ

(515041025)

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Tez Danışmanı : Prof.Dr. Ümit TUNCA (İ.T.Ü.)

Diğer Jüri Üyeleri : Doç.Dr. İsmail YILMAZ (İ.T.Ü.)

Doç.Dr. Nergis ARSU (İ.T.Ü.)

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LIST of SYMBOLS

ATRP	**:** Atom Transfer Radical Polymerization
SFRP	**:** Stable Free Radical Polymerization
RAFT	**:** Reversible Addition-Fragmentation Chain Transfer Polymerization
St	**:** Styrene
MMA	**:** Methyl methacrylate
R_m and R_n	**:** Propagating Radical
P_n and P_m	**:** Terminated Macromolecules
LFRP	**:** Living Free Radical Polymerization
CTA	**:** Chain Transfer Agent
TEMPO	**:** 2, 2, 6, 6- Tetramethylpiperidinoxy
PDI	**:** Polydispersity
PRE	**:** Persistent Radical Effect
M_t^n	**:** Transition metal
L	**:** Ligand
M_w/M_n	**:** The Molecular Weight Distribution
k_a	**:** Rate constant of activation
k_d	**:** Rate constant of deactivation
k_p	**:** Rate constant of propagation
DVB	**:** Divinylbenzene
THF	**:** Tetrahydrofuran
DMAP	**:** 4-dimethylaminopyridine
DCC	**:** *N*,*N*-dicyclohexylcarbodiimide
BPO	**:** Benzoyl peroxide
DPTS	**:** 4-dimethylamino pyridinium-4-toluene sulfonate
DPE	**:** Diphenyl ether
PMDETA	**:** *N*,*N*,*N*′,*N*″,*N*‴- pentamethyldiethylenetriamine
GPC	**:** Gel Permeation Chromotography
IR	**:** Infrared Spectrophotometer
NMR	**:** Nuclear Magnetic Resonance Spectroscopy

SYNTHESIS OF PMMA-*b*-PS CONTAINING A CROWN ETHER UNIT AT FOCAL POINT VIA COMBINATION OF ATRP AND NMP ROUTES

SUMMARY

The synthesis of well-defined copolymers is usually achieved by a living polymerization technique. Controlled/ "Living" Radical Polymerization processes have proven to be versatile for the synthesis of polymers with well-defined structures and complex architectures. Among the CRP processes, Atom Transfer Radical Polymerization (ATRP) and Nitrox Mediate Polymerization (NMP), are the most efficient methods for the synthesis of special block copolymers and polymers with complex architectures. Both, ATRP and NMP methods based on the fast equilibrium between active and dormant chains, actually it is the main effect to obtain controlled structure.

One of the advantageous of controlled radical polymerization techniques such as ATRP and NMP is that the molecular weight and the chain end functionality can be controlled. The wide range of functionality can be introduce into the polymer chain and this leads to the synthesis of well-defined copolymers by a sequential two-step or one pot method without any transformation or protection of initiating sites.

In this study, by using a novel miktofunctional initiator, we prepared poly(methyl methacrylate-*b*-polystyrene (PMMA-*b*-PS) copolymer with one crown ether unit at the focal point, via combination of ATRP and NMP routes. In addition, the complexation of PMMA-*b*-PS copolymer with potassium picrate (K^+ picrate) as template was studied

ATRP VE NMP YÖNTEMLERİ İLE CROWN ETER BAĞLANTI NOKTASI İÇEREN KOPOLİMERLERİN SENTEZİ

ÖZET

AB tipli kopolimerlerin sentezi genellikle yaşayan polimerizasyon yöntemiyle gerçekleştirilmektedir. Kontrollü/ "Yaşayan" Polimerizasyon yöntemlerinin iyi tanımlanmış ve kompleks yapılı polimerlerin sentezinde birçok açıdan faydalar sağladığı bilinmektedir. Kontrollü/ "Yaşayan" Radikal Polimerizasyon yöntemlerinin arasında Atom Transfer Radikal Polimerizasyonu (ATRP) ve Kararlı Serbest Radikal Polimerizasyonu (NMP) özel blok kopolimerler ve yıldız polimerler gibi kompleks yapılı polimerlerin sentezinde en etkili yöntemlerdir. ATRP ve NMP metodlarının her ikiside aktif ve kararlı zincirler arasındaki hızlı dinamik dengeye dayanır ki kontroüde sağlayan aslında budur.

ATRP ve NMP gibi kontrollü polimerizasyon tekniklerinin bir avantajı da elde edilen polimerin molekül ağırlığının ve zincir uç grubu fonksiyonalitesinin kontrol edilebilir olmasıdır. Bu teknikler sayesinde polimer uç gruplarına çok çeşitli fonksiyonellikler kazandırılabilir ki bu da herhangi bir transformasyon reaksiyonu gerektirmeden iyi tanımlı polimerlerin eldesine izin verir.

Bu çalışmada, iki fonksiyonel gruba sahip ve crown eter içeren bir başlatıcı sentezlenmiştir. Sentezlenen bu başlatıcı sırasıyla ATRP-NMP polimerizasyon yöntemi kullanılarak, crown ether bağlantı noktası içeren PMMA-*b*-PS kopolimerinin hazırlanmasında başarıyla kullanılmıştır. Bu çalışmada ayrıca, polimetilmetakrilat (PMMA) ın kinetik çalışması yapılmıştır. GPC (Jel Geçirgenlik Kromotografisi) ve ^{1}H-NMR dan elde edilen sonuçlar başarıyla gerçekleştiğini göstermiştir.

1. INTRODUCTION

Recently, the controlled/"living" radical polymerizations have been used for the synthesis of well-defined, narrow polydispersity polymers [1,2]. Among them, metal catalyzed free radical polymerization, often called atom transfer radical polymerization (ATRP) and nitroxide- mediated free radical polymerization are more versatile methods for the controlled radical polymerization of various types of monomers. One of the advantages of controlled/"living" radical polymerizations when compared with conventional free radical polymerization is the control of the molecular weight, narrow molecular weight distribution and chain end functionality.

Pedersen's [56] pioneering invention on macrocyclic polyethers (crown ethers) led to supramolecular chemistry. The crown ethers and the related compounds have attracted more interest because of their potential for a large number of applications. The reason for their current development is based on their powerful and selective complexation properties. The syntheses and properties of crown ethers and their large number of derivatives have been studied extensively [56,69].

To date, a variety of polymers containing crown ether units have been described [70,71] The crown ethers can be part of a main chain, pendant groups anchored to a polymer backbone, the end functional group of a macromolecular chain [70,71] or incorporated in a complex macromolecular structure such as star or dendrimeric polymers [72,73]. On the other hand, there have been few reports on the synthesis of

crown ether containing polymers obtained by using controlled/"living" polymerization methods [66,74].

In this manner, recently, Feng et al. prepared two bromo functional crown ether initiator and used it as an initiator in ATRP of various monomers.[66] Thus obtained polymers were self-assembled in the presence of potassium cations. Moreover, Gao et al. prepared two-armed polystyrene with a crown ether using a previous described initiator and investigated the complex effect of crown ether unit with Ag+ and Ag.[75] On the other hand, Gibson et al. first reported the preparation of the supramolecular star polymer based on pseudorotaxane complexation[66]. They introduced a paraquat moiety at end of every polystyrene chain obtained from NMP of styrene. It was as guest self-assembled with tris(crown ether) as host by a supramolecular coupling method.

In this study, by using a novel miktofunctional initiator, we prepared poly(methyl methacrylate-*b*-polystyrene (PMMA-*b*-PS) copolymer with one crown ether unit at the focal point, via combination of ATRP and NMP routes. In addition, the complexation of PMMA-*b*-PS copolymer with potassium picrate (K^+ picrate) as template was studied.

2. THEORETICAL PART

2.1. Conventional Free Radical Polymerizations

Free radical polymerizations are of significant importance in the industrial sector for a variety of reasons. First, many monomers capable of undergoing chain reactions are available in large quantities from the petrochemical sector [3]. In addition, free radical mechanisms are well understood and extension of the concepts to new monomers is generally straightforward. A third advantage of free radical routes is that the polymerization proceeds in a relatively facile manner: rigorous removal of moisture is generally unnecessary while polymerization can be carried out in either the bulk phase or in solution. As chain reactions, free radical polymerizations proceed via four distinct processes:

1. *Initiation*. In this first step, a reactive site is formed, thereby "initiating" the polymerization.

2. *Propagation*. Once an initiator activates the polymerization, monomer molecules are added one by one to the active chain end in the propagation step. The reactive site is regenerated after each addition of monomer.

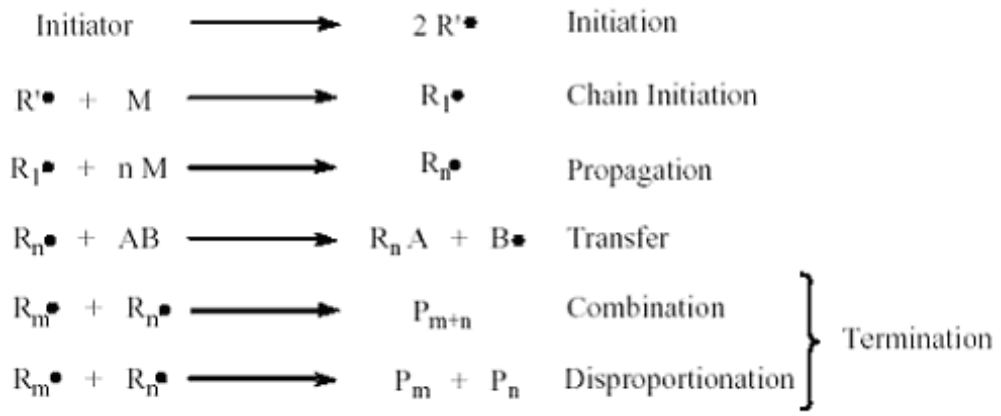
3. *Transfer*: occurs when an active site is transferred to an independent molecule such as monomer, initiator, polymer, or solvent. This process results in both a terminated molecule (see step four) and a new active site that is capable of undergoing propagation.

4. *Termination*. In this final step, eradication of active sites leads to "terminated," or inert, macromolecules. Termination occurs via coupling reactions of two active centers (referred to as combination), or atomic transfer between active chains (termed disproportionation).

The free radical chain process is demonstrated schematically below (2.1): $R^{\cdot}$ represents a free radical capable of initiating propagation; M denotes a molecule of monomer; R_m and R_n refer to propagating radical chains with degrees of

polymerization of *m* and *n*, respectively; AB is a chain transfer agent; and $P_n + P_m$ represent terminated macromolecules.

Because chain transfer may occur for every radical at any and all degrees of polymerization, the influence of chain transfer on the average degree of polymerization and on polydispersity carries enormous consequences. Furthermore, propagation is a first order reaction while termination is second order. Thus, the proportion of termination to propagation increases substantially with increasing free radical concentrations. Chain transfer and termination are impossible to control in classical free radical processes, a major downfall when control over polymerization is desired.



(2.1)

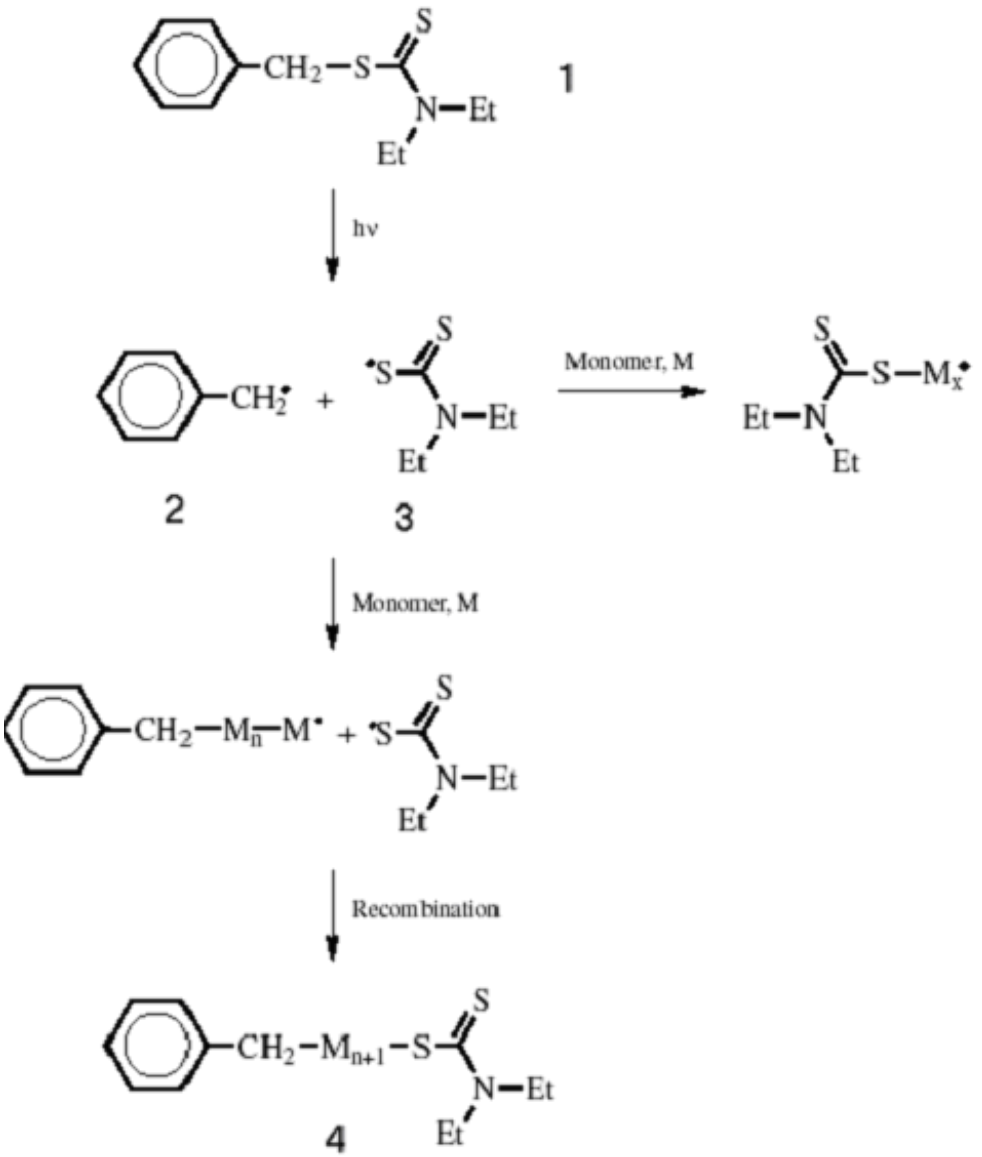
2.2. Controlled/ ‘‘Living” Free Radical Polymerizations

Living polymerization was first defined by Szwarc[4] as a chain growth process without chain breaking reactions (transfer and termination). Such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). Additional prerequisites to achieve these goals include that the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [5-7]. It has been suggested to use a term controlled polymerization if these additional criteria are met [8]. This term was proposed for systems, which provide control of MW and MWD but in which chain breaking reactions continue to occur as in RP. However,

the term controlled does not specify which features are controlled and which are not controlled. Another option would be to use the term ‘‘living’’ polymerization (with quotation marks) or ‘‘apparently living,’’ which could indicate a process of preparing well-defined polymers under conditions in which chain breaking reactions undoubtedly occur, as in radical polymerization [9,10]. The term controlled/living could also describe the essence of these systems [8].

2.2.1. Iniferter

Iniferters (initiator–transfer agent–terminator) was first introduced by Otsu in 1982 and constituted the first attempt to develop a LFRP technique[11]. In this case, disulfides, 1, including diaryl and dithiuram disulfides, were proposed as photochemical initiators where cleavage can occur at the C-S bond to give a carbon-based propagating radical, 2, and the mediating thio-radical, 3 (Scheme 2.2).



(2.2)

While the propagating radical, 2, can undergo monomer addition followed by recombination with the primary sulfur radical, 3, to give a dormant species, 4, it may also undergo chain transfer to the initiator itself. As opposed to conventional free-radical polymerization, which results in high molecular weights, even at low conversion, this technique provides rudimentary characteristics of typical living systems, such as a linear increase in molecular weight with conversion.

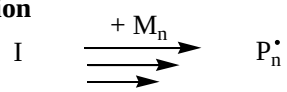
2.2.2. Reversible Addition – Fragmentation Chain Transfer Reactions (RAFT)

Another mechanism, RAFT, for achieving living character is free-radical polymerization with reversible chain transfer [12]. The initiation system consists of a

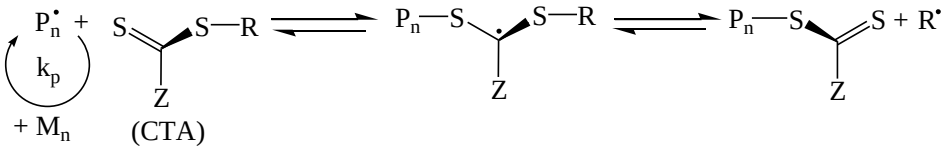
standard free-radical initiator and a suitable thiocarbonylthio compound, which acts as highly efficient reversible addition–fragmentation chain transfer agent (CTA agents) and provides the polymerization with living characteristics.

In RAFT, the CTA acts as so-called "trapping agent" because it is transferred between the active and the trapped chain. These trapped chain, usually called dormant chains, are unable to propagate but also unable to terminate. Because chain termination is bimolecular reaction, so the termination rate is second order with respect to the radical concentration [$M_m\cdot$]. While chain propagation is first order to the radical concentration [$M_m\cdot$] and proportional to the monomer concentration [M]. So we can see the termination rate is far less than propagation rate. Therefore, the probability of termination is largely reduced with respect to that of chain growth. So this leads to a negligible amount of terminated chains at the end of process. This is why RAFT has a living character. However, since terminations are definitely present, so this polymerization is also referred to as living radical polymerization. The resultant polymer has a controlled molecular weight and narrow molecular weight distribution [13, 14].

Initiation

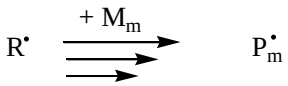


Chain Transfer (Addition/Fragmentation)

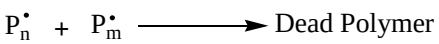


(2.3)

Reinitiation/Propagation



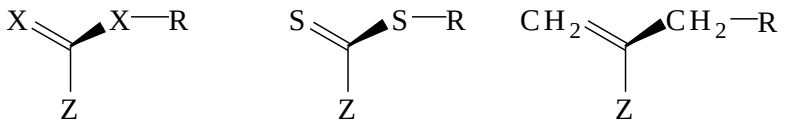
Termination



RAFT involves a reversible chain transfer in which a dithioester behaves as a chain transfer agent (CTA). The CTA reacts with either the primary radical or a propagating chain, forming a new CTA and eliminating R·, which re-initiated

polymerization. The dithioester is transferred between the active and dormant chains, thus maintaining the living character of the polymerization. As seen from scheme (2.3), RAFT mechanism differs from normal free radical polymerization mechanism by having a chain transfer agent, which leads to addition-fragmentation, re-initiation/propagation and chain equilibrium between chain radical and a new CTA. Because the addition-fragmentation chain transfer process is reversible, so the process is called reversible addition-fragmentation chain transfer polymerization (RAFT).

A RAFT process is actually a kind of degenerative chain transfer reaction, in which activation and deactivation occur at the same time or an active site migrates from one chain to another. So the key to successful RAFT polymerization is to select highly efficient CTA (2.4a). The polymerization is carried out in the presence of thiocarbonylthio of general structure (2.4b) and results in the formation of end-functionalized polymers. Z should activate the C=S double bonds [12, 15]. So the rate of addition and fragmentation must be fast relative to the rate of propagation. This leads to rapid consumption of the RAFT agent and fast equilibrium of the dormant and active chain. On the other hand, the leaving group R must be easily to leave and be able to re-initiate polymerization for the chain reaction to proceed. Generally, R should be a good homolytic leaving group when compared to polymer chain. Macromonomers (2.4c), where X is CH_2 can also function as RAFT agents [16, 17, 18, and 19].



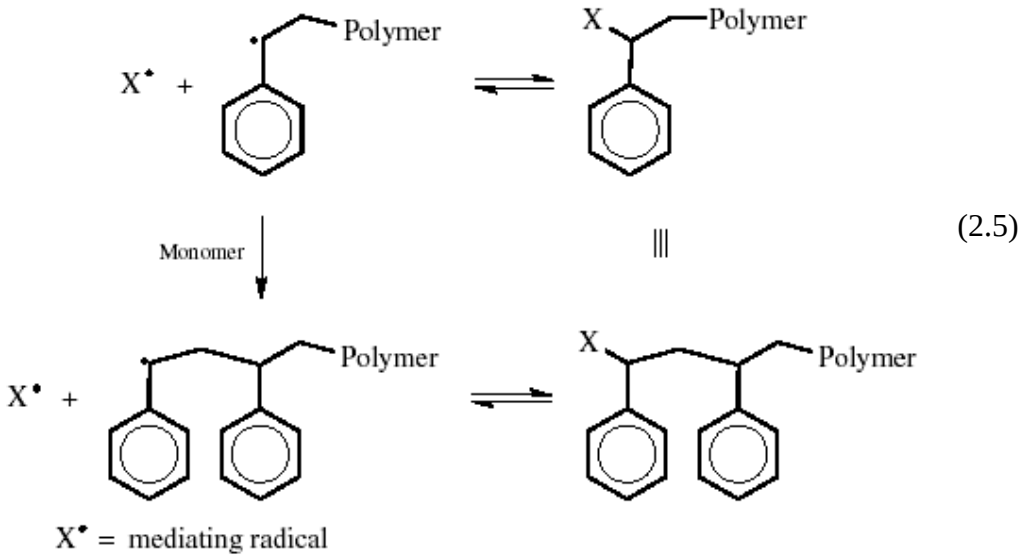
(a) (b) (c) (2.4)

The greatest advantage to RAFT is the incredible range of polymerizable monomers practiced in both organic solvents and aqueous media (including water) under a broad range of experimental conditions. As long as the monomer can undergo radical polymerization, the process will most likely be compatible with RAFT. However, there are many major drawbacks that arise when using this process. The dithio end groups left on the polymer give rise to toxicity, color, and odor and their removal or displacement requires radial chemistry. Also, the RAFT agents are expensive and not commercially available. Another drawback is that the process requires an initiator,

which can cause undesired end groups and produce too many new chains which can lead to increased termination rates [20].

2.2.3. Nitroxide-Mediated Living Radical Polymerizations

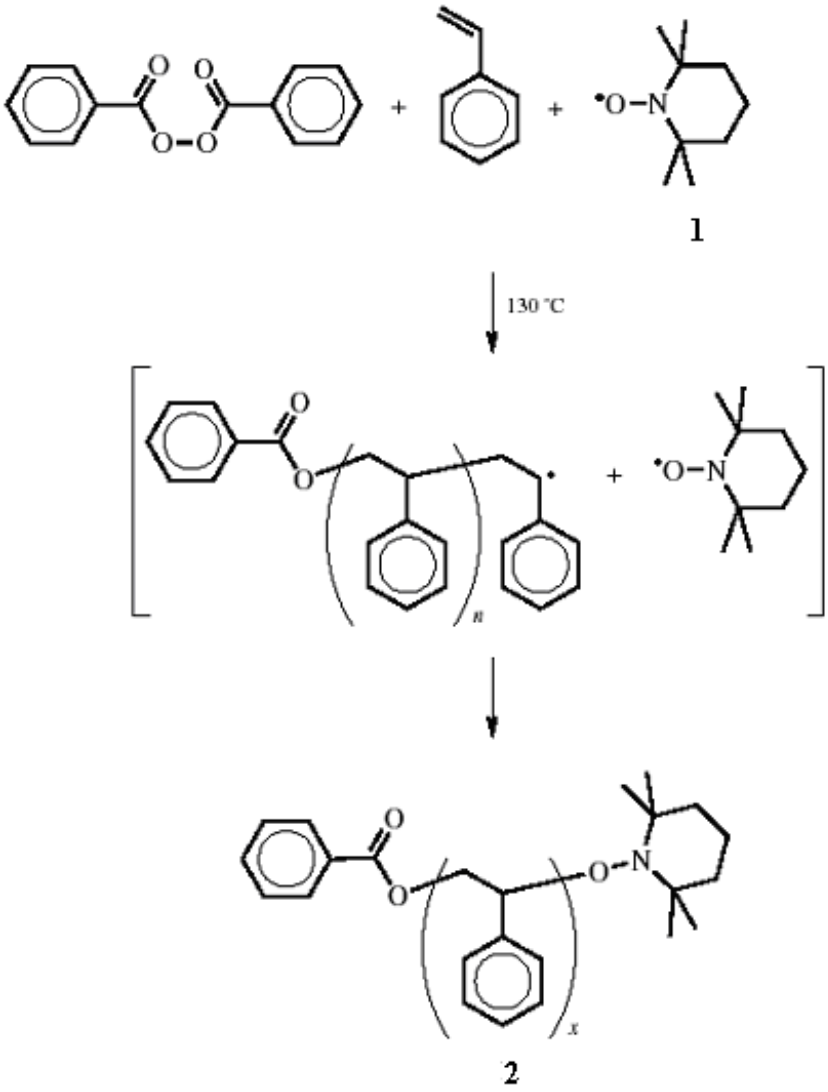
This pioneering work was one of the seminal contributions that provided the basis for the development of LFRP, and it is interesting to note the similarity between the iniferter mechanism outlined in Scheme 2.2 and the general outline of a living free-radical mechanism (Scheme 2.5). In this general mechanism, the reversible termination of the growing polymeric chain is the key step for reducing the overall concentration of the propagating radical chain end. In the absence of other reactions leading to initiation of new polymer chains (i.e., no reaction of the mediating radical with the vinylic monomer), the concentration of reactive chain ends is extremely low, minimizing irreversible termination reactions, such as combination or disproportionation. All chains would be initiated only from the desired initiating species and growth should occur in a pseudoliving fashion, allowing a high degree of control over the entire polymerization process with well-defined polymers being obtained. The identity of the mediating radical, $X^{\bullet}$, is critical to the success of living free radical procedures and a variety of different persistent, or stabilized radicals have been employed [21–25]. However the most widely studied and certainly most successful class of compounds are the nitroxides and their associated alkylated derivatives, alkoxyamines. Interestingly, the development of nitroxides as mediators for radical polymerization stems from pioneering work by Solomon, Rizzardo, and Moad into the nature of standard free-radical initiation mechanisms and the desire to efficiently trap carbon-centered free radicals [26].



(2.5)

2.2.3.1. Bimolecular Process

The second seminal contribution that proved conclusively that living free-radical polymerizations are a viable synthetic methodology was a report from the group of Georges at XEROX describing the preparation of low polydispersity polystyrene (PDI = 1.20) and the subsequent synthesis of polystyrene-based block copolymers [27]. The key feature of this work was the realization that, while nitroxides are polymerization inhibitors at low temperatures, hence their use by Solomon to trap polymerization intermediates, at elevated temperatures they may act as polymerization mediators, not inhibitors. By increasing the temperature to 130 ^{o}C and conducting the polymerizations in the bulk, a system consisting of benzoyl peroxide and a stable nitroxide, TEMPO **1**, in the molar ratio of 1.3 : 1, gave polystyrene derivatives, **2**, by a living process in which the molecular weight increased in a linear fashion with conversion (2.6). Even more startling were the polydispersity



1

2

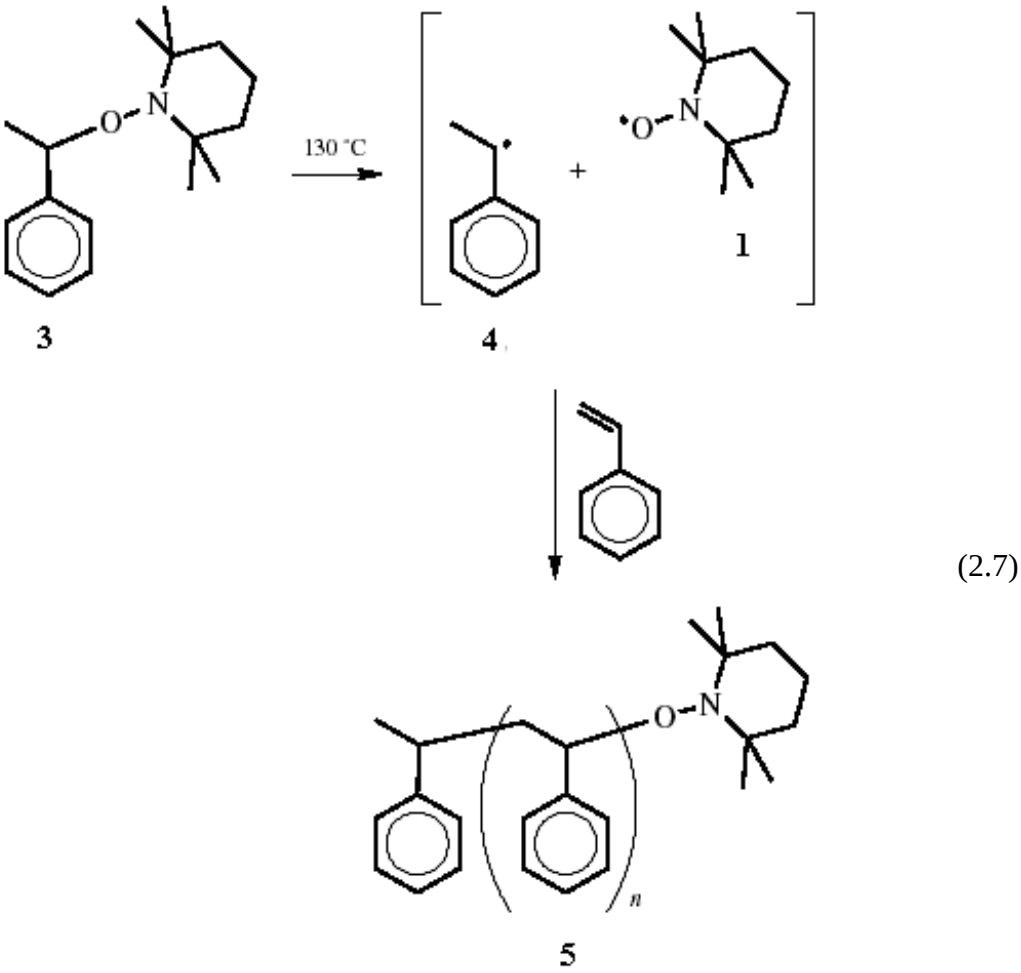
(2.6)

values for **2**, PDI =1.2, which were significantly lower than the theoretical lower limit for a free-radical process of 1.5 and the typical values of ~2.0 for free-radical systems.

2.2.3.2. Unimolecular Initiators

The structure of these initiators was based on the alkoxyamine functionality that is present at the chain end of the growing polymer during its dormant phase. The C-O bond of the small-molecule alkoxyamine derivative, **3**, is therefore expected to be thermolytically unstable and decompose on heating to give an initiating radical, namely, the a-methyl benzyl radical, **4**, as well as the mediating nitroxide radical, **1**, in the correct 1:1 stoichiometry (seen in 2.7). Following initiation the polymerization would proceed as described previous for the bimolecular case to give the polystyrene

derivative, **5**. The advantage of the unimolecular initiator approach is that the structure of the polymers prepared can be controlled to a much greater extent. Since the number of initiating sites per polymerization is known, the molecular weight can be accurately controlled. The unimolecular initiator can also be functionalized to permit the controlled introduction of functional groups at the chain ends of the macromolecules.

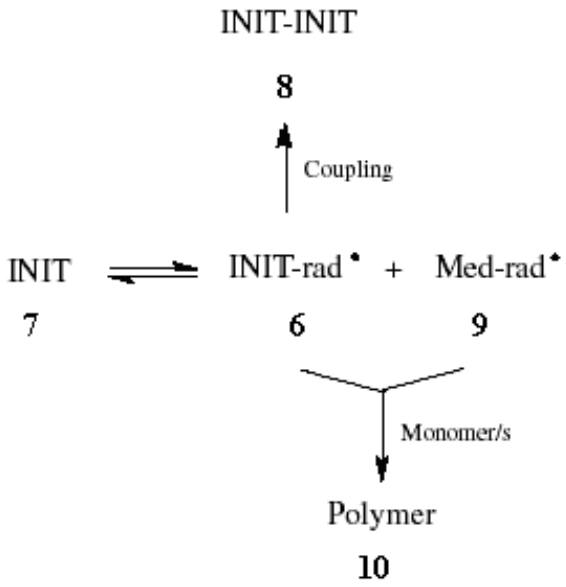


(2.7)

2.2.3.3. Mechanistic and Kinetic Features

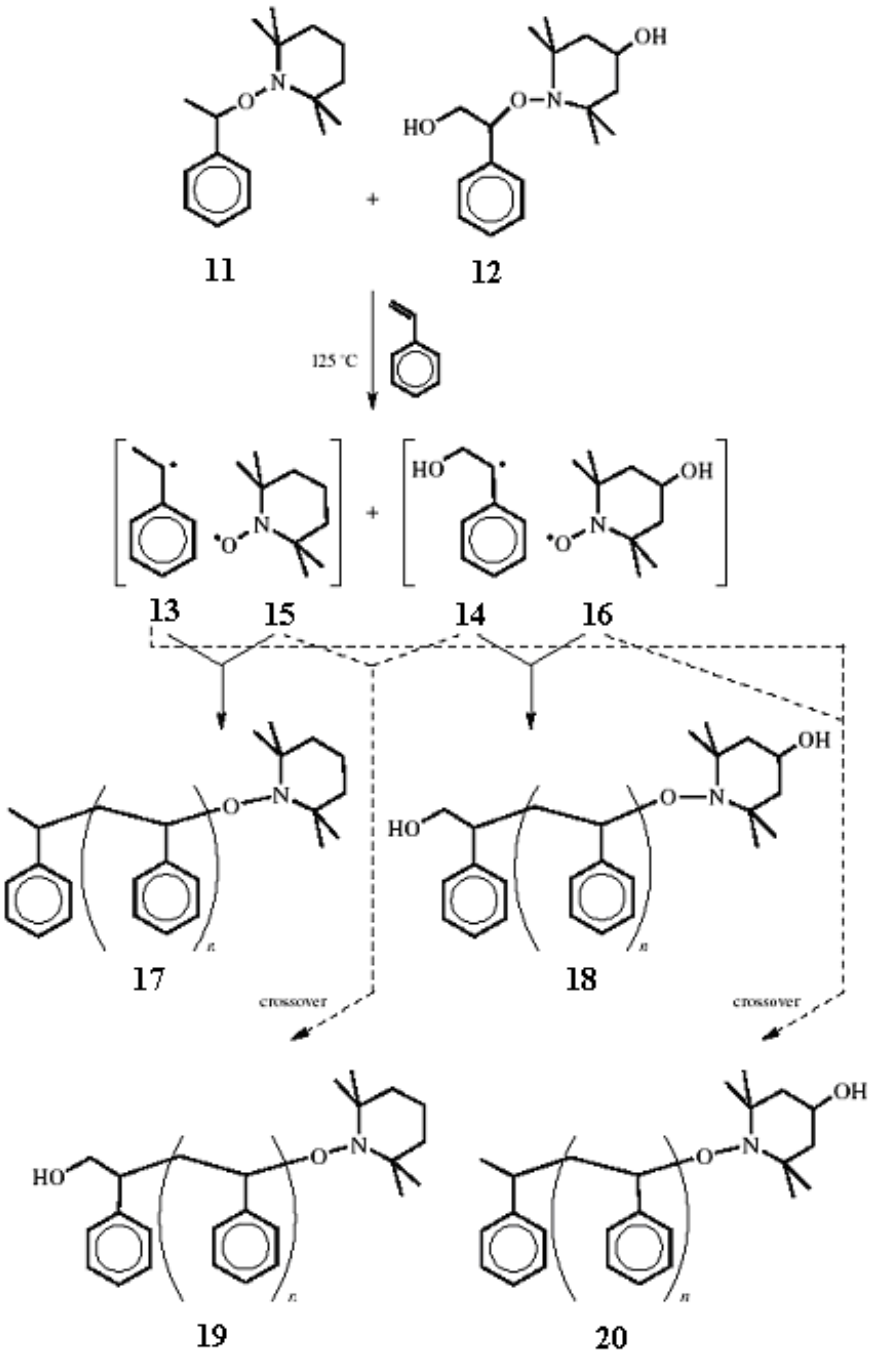
The key kinetic feature of nitroxide mediated living free-radical polymerization is the operation of a special phenomenon, termed the persistent radical effect (PRE). Fischer has developed the analytic equations for the polymerizations rates and for the polydispersities of the resulting polymers that have been shown to effectively model LFRP [28,29].

In the initial stages of the polymerization, a small fraction of the initiating radicals, 6, formed from decomposition of the initiator, **7**, undergo radical–radical coupling. This leads to a terminated molecule/oligomer, **8**, and the resulting removal of two initiating radicals from the system. At this early stage of the polymerization, this is a facile reaction since the diffusing radicals are sterically small and the reaction medium is not viscous. However, by nature, the mediating radical, or persistent radical, **9**, does not undergo coupling and so a small increase in the overall concentration of **9** relative to the propagating/initiating radical, **6**, occurs.



(2.8)

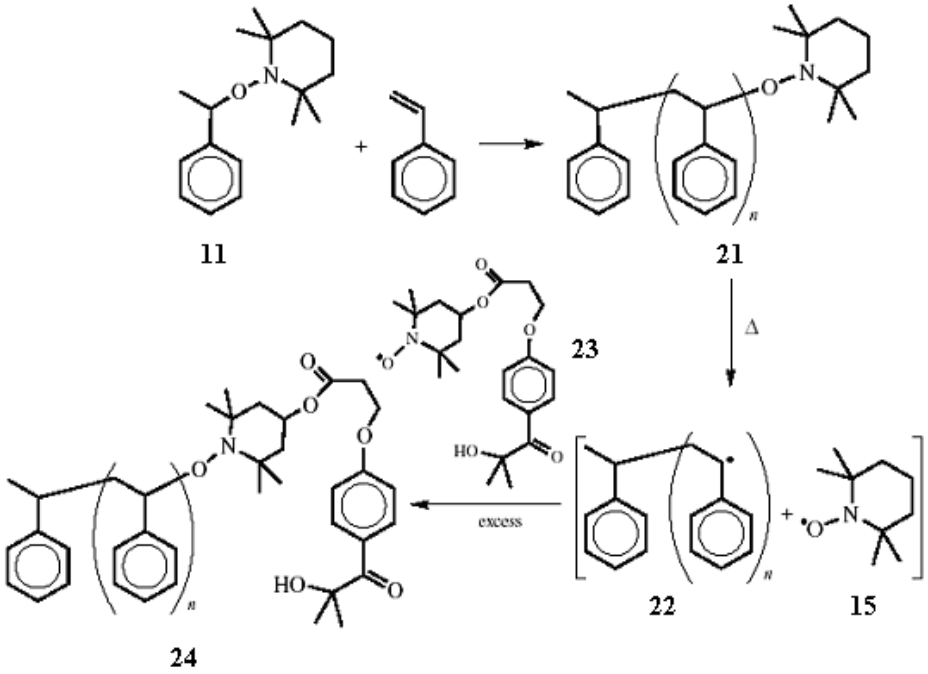
This increased level of **9** is self-limiting since a higher concentration leads to more efficient formation of the dormant chain end, **10**, and a decrease in the amount of radical–radical coupling (see 2. 8) leading to the persistent radical effect (PRE) and to the eventual control over the polymerization process. The nature of the equilibrium between the dormant system, **10**, and the pair of radicals, **6** and **9**, has been probed and exploited by a number of groups. The exact nature of the radical pair, caged versus freely diffusing, was probed by a series of crossover experiments [30,31].



(2.9)

The design of crossover experiments to probe the potential diffusion of the mediating radical from the propagating chain end during ‘‘living’’ free-radical polymerizations involves the use of two structurally similar alkoxyamines, which differ only in their substitution pattern. One derivative is unfunctionalized, **11**, while the other alkoxyamine, **12**, contains two hydroxy groups, one is attached to the TEMPO unit while the second is located at the beta-carbon atom of the ethylbenzene unit. If a 1 : 1

mixture of **11** and **12** is used to initiate the ‘‘living’’ free-radical polymerization of styrene, homolysis of the carbon–oxygen bond of **11** and **12** will lead to four radical species. Each radicals produced is chemically different and constitutes a pair of initiating, or propagating, radicals, **13** and **14**, and a pair of structurally similar mediating nitroxide radicals are produced, TEMPO, **15**, and 4-hydroxy-TEMPO, **16**. If no escape of the mediating nitroxide radical from propagating chain end occurs, only two polystyrene derivatives will therefore be formed; **17** and **18**. In contrast, if radical crossover does occur and the mediating nitroxide radicals are free to diffuse to the polymerization medium, four polystyrenes having different substitution **17–20**, will be obtained. Significantly, the experimental result from these crossover experiments revealed a statistical mixture of all four products, even at low conversions, implying freely diffusing radicals (see 2.9). Turro[32] has elegantly taken advantage of this feature to develop a strategy for the facile preparation of chain-end functionalized macromolecules. In this approach a precursor polymer, **21**, is prepared from a standard unfunctionalized initiator, such as **11**, purified and then redissolved in a high-boiling-point solvent such as chlorobenzene and heated at 125^{o}C in the presence of a large excess of functionalized nitroxide, **23**. At this temperature the equilibrium between **22** and the two radicals is established and since the released nitroxide, **11**, is free to diffuse into the solution, exchange with the functionalized nitroxide, **23**, can occur leading to the desired chain end functionalized macromolecule, **24** (see 2.10).

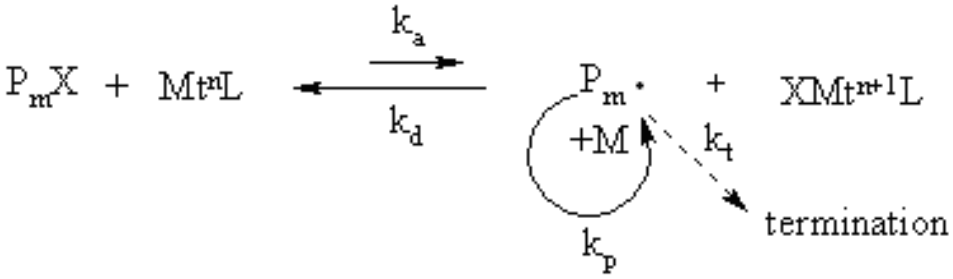


(2.10)

This strategy presents a number of advantages, reactive functional groups can be introduced under mild conditions, from the same precursor polymer a variety of differently tagged macromolecules can be prepared, and the same strategy can be applied to macromolecules of different architectures.

2.2.4. Atom Transfer Radical Polymerization (ATRP)

ATRP is one of the most versatile controlled radical polymerization method.This method utilizes a reversible halogen atom abstraction step in which a lower oxidation state metal (M_t^n complexed by ligands L) reacts with an alkylhalide (P_m-X) to generate a radical ($P_m^{\bullet}$) and a higher oxidation state metal complex ($XM_t^{n+1}L$). This radical then adds monomer to generate the polymer chain (k_p). The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and the lower oxidation state metal (k_d) as seen in (2.11). The molecular weight is controlled because both initiation and deactivation are fast, allowing for all the chains to begin growing at approximately the same time while maintaining a low concentration of active species. Termination cannot be totally avoided; however, the proportion of chains terminated compared to the number of propagating chains is small [33]. Several metal/ligand systems have been used to catalyze this process and a variety of monomers including styrene, methacrylates, and acrylonitrile have been succesfully polymerized [34-36].



(2.11)

The rate of ATRP is internally first order in monomer, externally first order with respect to initiator and activator, Cu(I),and negative first order with respect to deactivator, XCu(II). The actual kinetics depends on many factors including the solubility of activator and deactivator, their possible interactions, and variation of their structures and reactivities with concentrations and composition of the reaction medium.

One of the most important parameters in ATRP is the dynamics of exchange, especially the relative rate of deactivation. If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates leading to conventional, and not controlled, radical polymerization. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_d, and also with the concentration of deactivator, [XCu(II)]. They, however, increase with the propagation rate constant, k_p, and the concentration of initiator, $[RX]_o$. This means that more uniform polymers are obtained at higher conversion, when the concentration of deactivator in solution is high and the concentration of initiator is low. Also, more uniform polymers are formed when deactivator is very reactive and monomer propagates slowly (styrene rather than acrylate) [37].

2.2.4.1. Monomers

A variety of monomers have been succesfully polymerized using ATRP. Typical monomers include styrenes (meth) acrylates, (meth) acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the

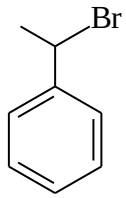
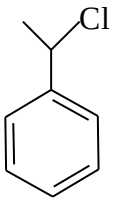
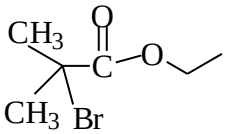
magnitude of the equilibrium constant ($K_{eq}=k_{act}/k_{deact}$) determines the polymerization rate.

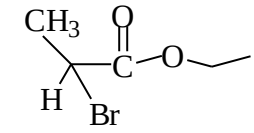
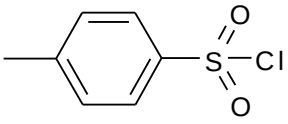
2.2.4.2. Initiators

The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a succesful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

In ATRP, alkylhalides (RX) are typically used as initiator and the rate of polymerization is first order with respect to the concentration of RX.To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. When X is either bromine or chlorine, the molecular weight control is the best. Flourine is not used because the C-F bond is too strong to undergo homolytic cleavage.

Table 2.1. The most frequently used initiator types in ATRP systems

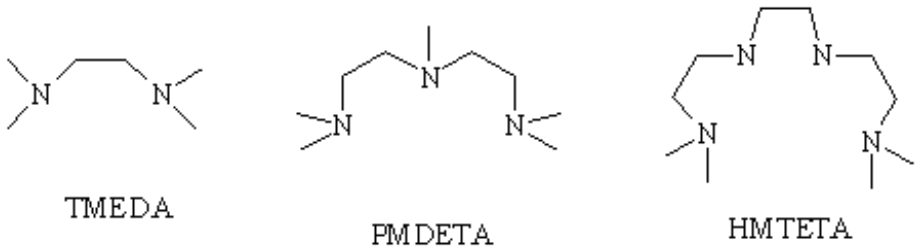
Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methyl methacrylate

 Ethyl-2-bromo propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methyl methacrylate

2.2.4.3. Ligands

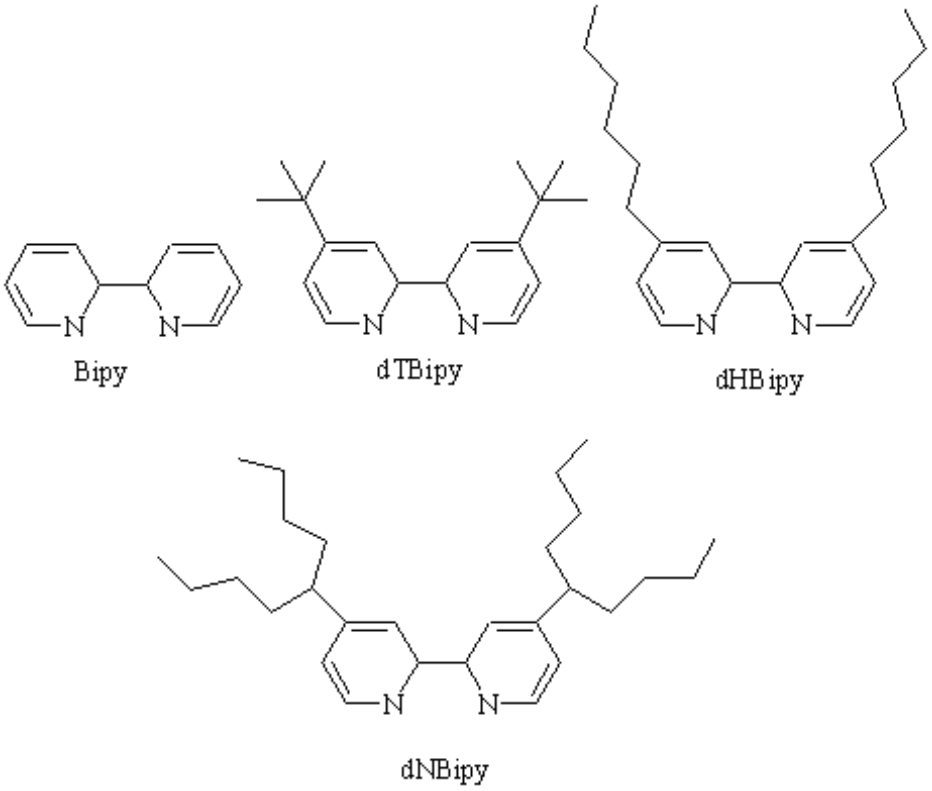
The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer. There are several guidelines for an efficient ATRP catalyst. First fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as β-H abstraction or reduction/oxidation of the radicals.

Nitrogen based ligands:



(2.12)

Derivatives of 2,2-bipyridine:



(2.13)

The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine(HMTETA), tris[2-(dimethylamino) ethyl]amine (Me-TREN) and alkylpyridylmethanimines are also used.

2.2.4.4. Transition Metal Complexes

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisities for an efficient transition metal catalyst. First, the metal center must have at least two readily accesible oxidation states separated by one electron. Second the metal center should have reasonable affinity toward a halogen. Third the coordination sphere around the metal should be expandable upon oxidation to selectively accomodate a (pseudo)-halogen. Fourth the ligand should complex the metal relatively strongly.

The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$/ $Al(OR)_3$.

2.2.4.5. Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer.

2.2.3.6. Kinetics of ATRP

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator (CuX_2 / Ligand).

The rate equation of ATRP is formulated in discussed conditions and given in (2.14).

$$R_p = k_{app}[M] = k_p[P.][M] = k_p K_{eq}[I]_0 \frac{[Cu(I)]}{[Cu(II)X]}[M] \qquad (2.11)\ (2.14)$$

Results from kinetic studies of ATRP for styrene, methyl acrylate (MA), and methyl methacrylate (MMA) under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations.

If the deactivation does not occur, if it is too slow ($k_p >> k_d$), there will be no difference between ATRP and the classical redox reactions and the termination and transfer reactions may be observed. To gain better control over the polymerization, addition of one or a few monomers to the growing chain in each activation step is desirable. Molecular weight distribution for ATRP is given in (2.15).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d[RX]_0}{k_p[XCu^{II}]}\right)\left(\frac{2}{p} - 1\right) \qquad (2.12)$$

p= poymerization yield
$[RX_0]$=concentration of the functional polymer chain
$[XCu^{II}]$=concentration of the deactivators
k_d=rate of deactivation
k_p=rate of propagation (2.15)

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

a) For the smaller polymer chains, higher polydispersites are expected to be obtained because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.

b) For the higher ratios of k_p / k_d, higher polydispersities (molecular weight distributions) are usually obtained.

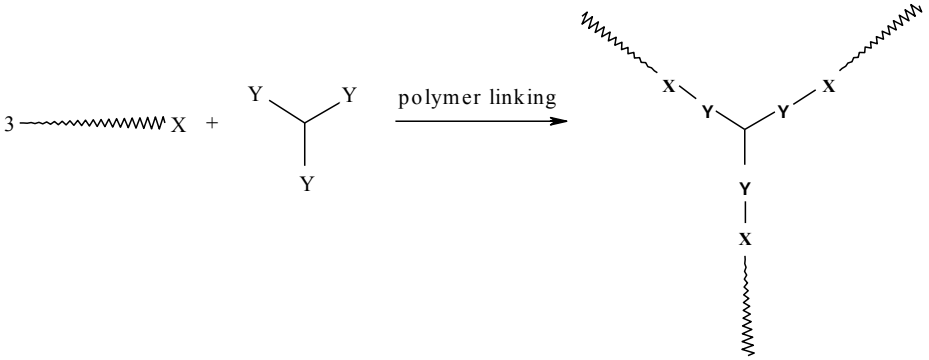
c) Resulting molecular weight distribution decreases as the concentration of the deactivators increases.

2.3. Star Polymers

Branched polymers of controlled architecture have been designed in order to get a better understanding of the relationship between their topology and their unique solution and bulk properties, as compared to linear polymers. Among the branched structures, star polymers represent the most elementary way of arranging the subchains since each star contains only one branching point [38]. The interest in star shaped polymers stems from their unique-spatial shapes, lower viscosity compared with that of linear polymers with similar molecular weights and possible processing advantages due to their compact structure [39]. Star polymers have found applications in various areas (rheology modifiers, pressure sensitive adhesives, etc.) [40].

2.3.1. Stars by the Arm-First Method

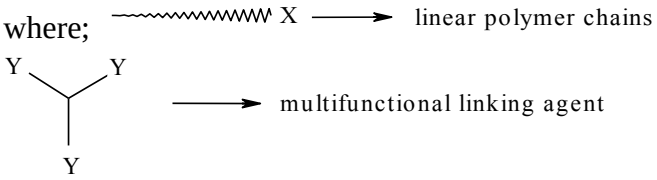
This technique involves the synthesis of preformed arms, usually through living polymerization followed by reaction with a multifunctional linking agent[41-43]. Schematic representation of star formation by the “arm-first method” is shown in (2.16).



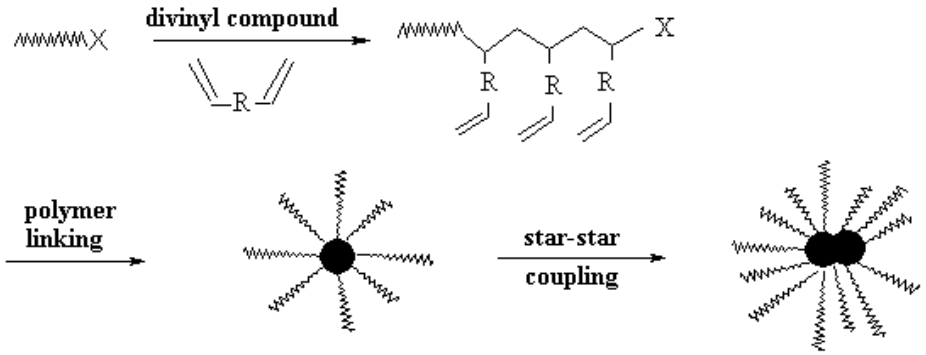
(2.13)

(2.16)

where;



Star formation by using the arm first technique also involves the use of divinyl coupling reagents such as divinylbenzene (DVB) as a multifunctional linking agent. Initially, a few units of the divinyl coupling reagents are added to the macroinitiator chain ends to form short block copolymers.



(2.17)

The block copolymers containing the divinyl units then start to react with each other to form cross-linked cores, and this leads to the formation of star polymers. Finally star-star coupling can occur, leading to the formation of higher molecular weight stars. The proposed mechanism for the star polymer formation in the presence of a divinyl coupling reagent is presented in (2.17) [44].

Coupling of monofunctional living chains with a difunctional reagent was first applied to living anionic polymerization. A similar approach has also been succesful with ATRP. There are several parameters in an ATRP that should be controlled carefully in order to maximize the yield of stars and prevent star-star coupling reactions. Some detailed studies have been carried out on the coupling of

monofunctional polystyrenes and polyacrylates with (DVB) and di(meth)acrylates to prepare star polymers and the following guidelines have been developed:

- The ratio of difunctional reagent to growing chains seems to be optimal in the range of 10-20
- Monomer conversion (or reaction time) has to be carefully controlled and stopped before star-star coupling occurs.
- Higher yields of stars are observed for polyacrylates than for polystyrenes. This may be attributed to a higher proportion of terminated chains in styrene polymerization.
- The choice of the difunctional reagent is important and reactivity should be similar to, or lower than that of the arm-building monomers.
- Halogen exchange slightly improves efficiency of star formation.
- Solvent, temperature, catalyst concentration should be also optimized [45].

Some of the recent studies on star synthesis by the arm-first method are described below: An original study based on the arm-first approach was reported by Fraser et al.[46], who synthesized 2,2-bipyridyl- carrying PS and PMMA chains by ATRP, which they managed to chelate onto a hexadendate Fe(II)- based complex to form corresponding star-like polymers, thus containing a metallic core.

To derive their PS stars, Matyjaszewski et al.[44] used a preformed PS macroinitiator obtained by ATRP that was allowed to react with various divinylic monomers, in the presence of Cu/Br dipyridyl in anisole at 110 ^{0}C.A ratio of 5:15 between divinylbenzene and PS macroinitiator was found to be optimal for the star formation. Other experimental parameters such as the choice of solvent, the addition of Cu(II), and the reaction time were found to be crucial for the formation efficient star formation.

2.3.2. Stars by the Core-First Method

The core-first approach has come to maturity after it was shown in the1990s that stars of precise functionality could be obtained from multiionic initiators.

The core-first method involves the use of a multifunctional initiator, and the number of arms in the star polymer can be determined by the number of initiating sites on the initiator [39,47,48]. In this technique multifunctional initiators are used to grow

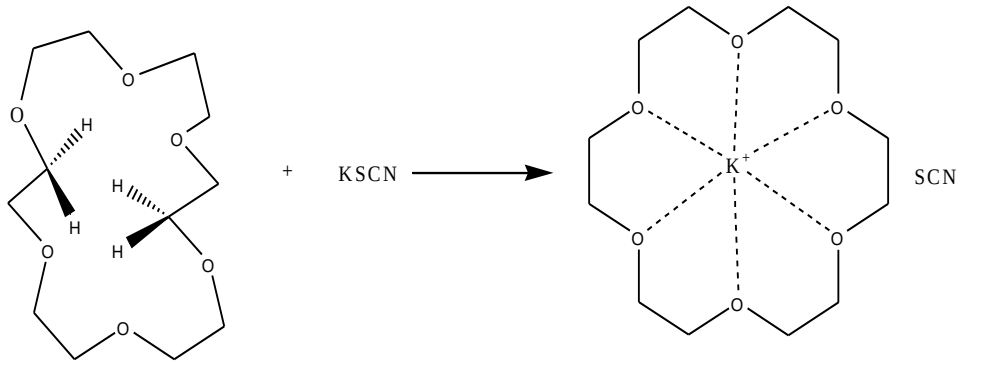
chains from a central core resulting in macromolecules with well-defined structures in terms of both arm number and length. Furthermore the reaction consists solely of stars in the absence of linear polymers [49]. Most of the star polymers were prepared by this technique.

The first report of the core-first technique described the hexakis (bromomethyl) benzene-initiated ATRP of styrene, methyl acrylate, and methylmethacrylate [50], but its use was rather limited due to poor solubility in the reaction media.

2.4. Crown Ethers

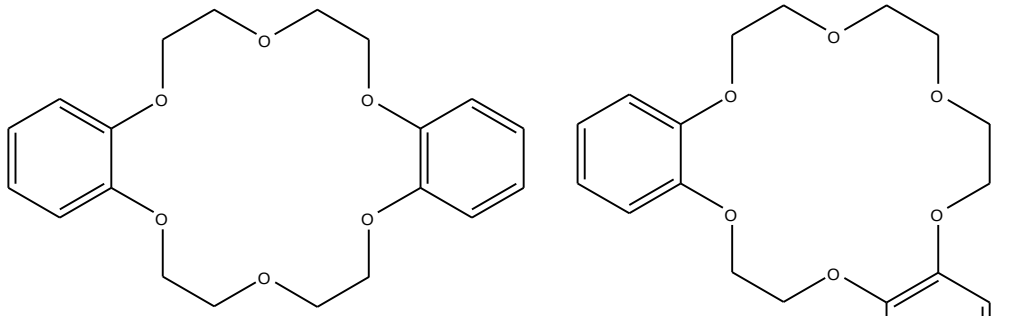
There are many development which predate Pedersen's first papers on crown ether chemistry [55,56]. Luttringhaus had made early preparation of crown ether compounds[57]. Moreover, the nitrogen macrocycles had been studied for decades prior to 1967 [58] and macrocyclic polyethers had been obtained years before from the cyclooligomerization of ethylene oxide [59]. At about the same time, cation complexation by naturally occurring polyoxygen containing species was established [60] and the 'self solvating base' described by Ugelstad [61] bear a striking resemblance to what it is called 'crown complexation'. But, nevertheless, the beginning of crown ether chemistry is generally dated from Pedersen's first disclosures in 1967 because many examples of these compounds were prepared and their potential as complexing agent was recognized by Pedersen.

The 'crown ether' term was first suggested by Pedersen and has been widely used [56]. It generally refers to macrocyclic polyethers having the ethyleneoxy unit as the basic repeating structure. When every third atom is oxygen, binding is obviously higher than when more carbons separate the hetero atoms. In addition, the unfavorable conformational interactions are reduced relative to the carbon analogs.



(2.18)

The nomenclature convention suggested by Pedersen [56] for the simple compounds involves two numbers. The first of these indicates the number of atoms in the macrocycle. The second number indicates how many hetero atoms are present in the ring.



(i)

dibenzo-18-crown-6

(ii)

an isomer of (i)

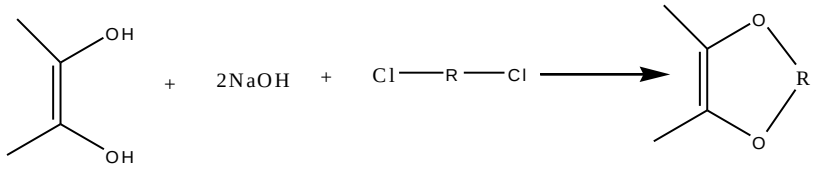
(2.19)

Compound (ii), above, is essentially 18-crown-6 into which two benzene have been fused, Pedersen suggested the name ‘dibenzo –18-crown-6’ to describe it. But, the name dibenzo does not adequately describe the relative positions of the benzene rings. Naturally, systematic names may be used for these compounds but such names have generally proved cumbersome. The systematic name for dibenzo-18-crown-6 is 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacycloactadeca-2,11-diene.

2.4.1. Synthesis of Crown Ethers

In the Pedersen's first paper on the synthesis of macrocyclic polyethers [55], he generalized the synthetic approaches. The four principal methods, for example, are V, W, X, and Y.

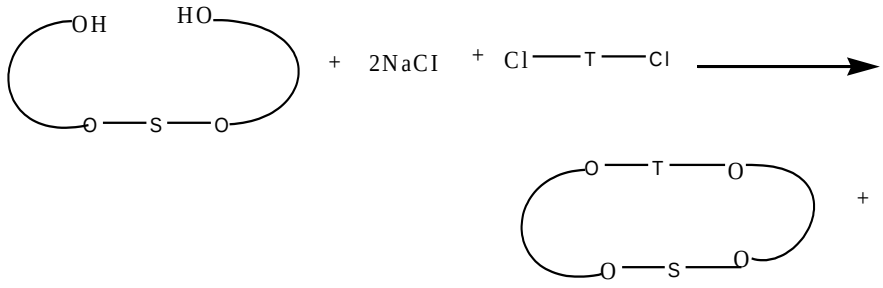
Method 'V' is shown in eq.(2.20). This corresponds the so-called 'one plus one' synthesis of crowns. The notion is that a single diol unit is allowed to react



(2.20)

with a single polyethylene glycol having leaving groups at each end. An example of this would be the synthesis of benzo-15-crown-5 from catechol and tetraethylene glycol dichloride. In addition, bases other than sodium hydroxide may be used and many cases are preferred. For aliphatic alcohols, potassium-t-butoxide has been used often, but NaH has been the base of choice. Although Pedersen successfully utilized cholorides as leaving groups in a number of synthesis, the most common choice of leaving group appears to be tosylate or methansulfonate.

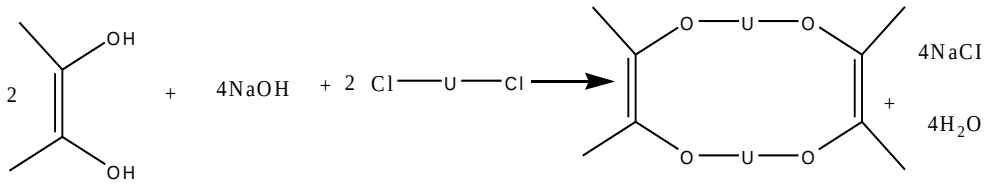
The second generally approach outlined by Pedersen is the so-called 'method W' in which the twohydroxyl groups are separated by a portion of the crown chain. A good example of this is the assembly of 18-crown-6 from triethylene glycol and triethylene glycol dichloride.



(2.21)

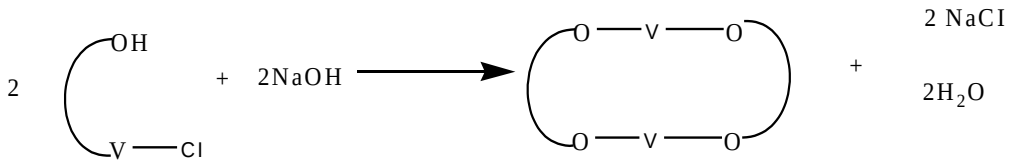
This method would be especially important when two halves of the crown unit are different.

Method ‘X’ is almost a corollary to method V since the stoichiometry is identical. In fact, it is not intention, but the size of crown which will determine the outcome of the reaction. For example, the synthesis of dibenzo-18-crown-6 is carried out by treating two equivalents of catechol with two equivalents pf diethylene glycol dichloride in the presences of four equivalents sodium hydroxide.



(2.22)

The fourth of Pedersen’s general methods is expressed as method Y. In this approach, a single unit may be both nucleophile and electrophile and react with the corresponding portion of its counterpart to yield a macrocycle.



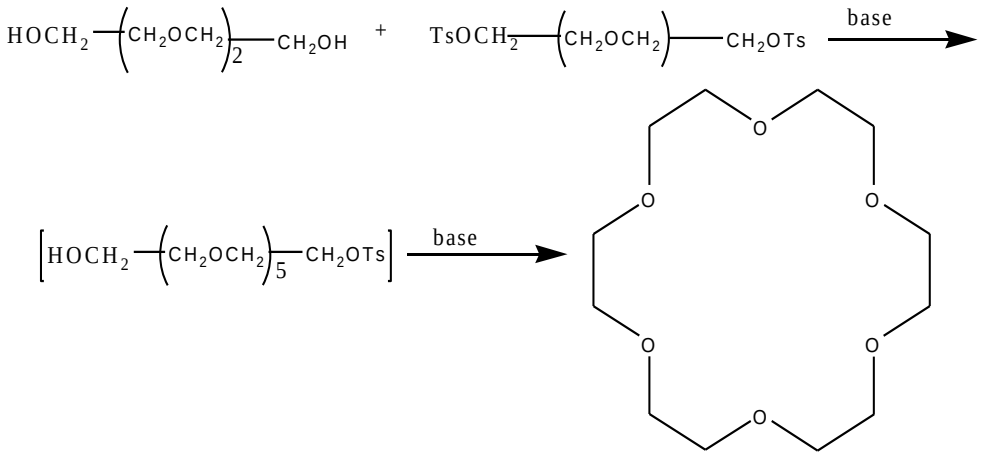
(2.23)

There are really two possibilities here. The first of these is that two units will react as illustrated, cyclize to afford a crown of half the size. It is precisely this approach which Pedersen used in the first synthesis of 18-crown-6.

These four methods suggested by Pedersen serve as a useful starting point for the consideration of other approaches and should certainly not be considered and overview of existing methodology.

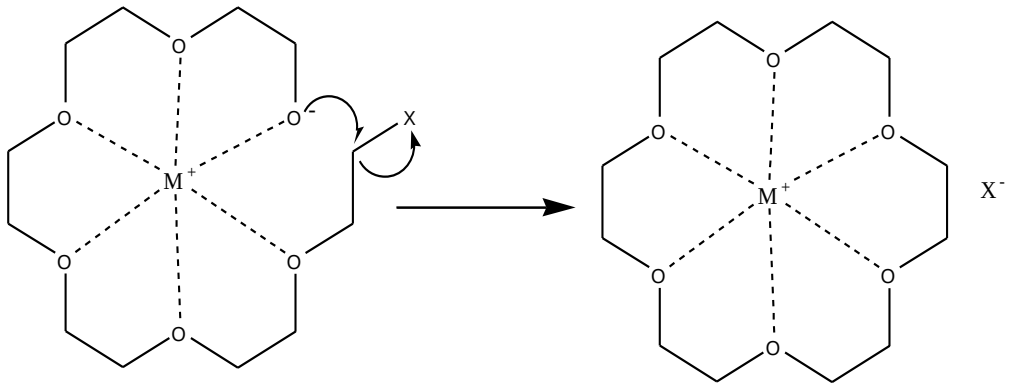
2.4.2 Template Effect and Mechanism of Complexation

Many of crown ether syntheses are one form or another of the Williamson ether synthesis Although the simplest example of such a reaction would involve an W-haloethylene glycol oligomer which undergoes intramolecular cyclization, it is more common for two new bonds to be formed in crown synthesis. An early example of the formation of a crown by a double-Williamson can be found in Dale's synthesis of 18-crown-6 [62]. The rather obvious chemical steps are shown in eq. (2.24)



(2.24)

The first C-O bond formation is probably not influenced strongly by the presence of a templating cation. Since it is not crucial for one end of chain to meet other rather than respecting with a different molecule. It is not necessary to superimpose either a template or dilution condition on the reaction to prejudice the statistics. In the second step, however, such a prejudicial condition is required. This is available in the form of an alkali metal cation for which the long ethyleneoxy chain has a certain affinity. Presumably, the cation is ion–paired with the alkoxide anion and the remainder of the chain wraps around it. Note that such a picture correspond to Ugelstad's 'self-solvating ' base [61]. The wrapping is illustrated in eq.(2.25) below



(2.25)

It is not clear exactly when association illustrated above actually take place. It is certainly involved by the final ring closure stage, but it seems reasonable to assume that there is some cation-glyme type interaction taking place from the instant of solution. The fact that wrapping occur in such a way that two ends of molecule are held in proximity, allows the reaction to be conducted at much higher concentrations than might otherwise be practical.

The first suggestion of a 'template effect' which has offered in the literature was made by Greene in 1972 [63]. The illustration of this concept is approximately that shown in eq.(2.25) above.

The optimization of template effect is probably achieved when the diameter of the cation corresponds most closely to the cavity diameter of the macrocycle being formed. Thus, for simple crown ether, Li^+, Na^+, and K^+ ions are clearly suited to templating the syntheses of 12-crown-4, 15-crown-5, 18-crown-6, respectively [64].

The formation of 'complex' by association of two or more chemical units is one of the most basic molecular prosses and of utmost importance in chemistry, physics and biology.

A host-guest complex, unlike covalent bonds, arises mostly through weak bond interactions (hydrogen bonding, metal-to-ligand bonding, pole-dipole binding forces, dipole-dipole binding forces, hydrophobic binding etc.)

The complexation process between a ligand, L, and a cation, M^{n+}, in solvent S may be represented by the general equation, where k_1, k_2 are defined as the rate

$$(L)_{solv} + (M^{n+}, mS) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (L, M^{n+})_{solv} + mS \qquad (2.26)$$

constant of formation and dissociation of a complex. The quotient of k_1/k_2 gives the stability constant, K_s. The thermodynamic stability constant K_{th} can be given by equation , where f_c, f_l, and f_m are the activity coefficients of the three

$$K_{th} = \frac{f_C\,[L, M^{n+}]}{f_L\,[L]\,f_M\,[M^{n+}]} \qquad (2.27)$$

Species present (complex, ligand, cation) since these coefficients are generally unknown, however, the stability constant K_s, based on the concentrations, are usually employed. K_s is an average stability constant for the system in

$$K_s = Kth \cdot \frac{f_L \cdot f_M}{f_C} = \frac{[L, M^{n+}]}{[L]\,f_M\,[M^{n+}]} \qquad (2.28)$$

Thermodynamic equilibrium on the basis of ligand conformation and complexation. The relationship between K_s and the free enthalpy of formation

$$\Delta G^0 = - RT \ln K_s. \quad (2.29)$$

2.4.3 Polymers Having Crown Ether Moieties

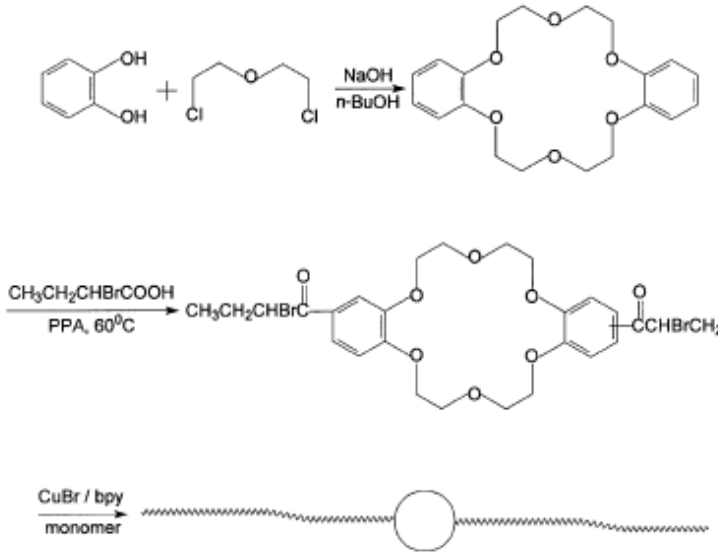
2.4.3.1 Self-assembly of two-armed polymer with a crown ether core [65]

Ordered porous materials are of great significance in the fields of bandgap materials, separation, catalysis, sensor, and microelectronic devices, etc. Many methods have been developed to create order in materials, including colloid templating , emulsion , block copolymer templating , surfactant templating , and water droplet templating, etc. These methods have been widely demonstrated to be reliable, versatile and effective in fabricating both two-dimensional (2D) and three-dimensional (3D) highly ordered porous materials. Their length scale is only limited to that of the templates.

Alternative strategies to create ordered materials come from self-assembly of molecules, especially macromolecules with tailored architectures. For example, block copolymers composed of unfavorable blocks can microphase-separate in melt to form body centered cubic (BCC) or hexagonally (HEX) ordered cylindrical structures which are widely used to produce porous materials with the dispersed phase etched. Particularly, the rod-coil copolymers, with one rod like block and one flexible block, can self-assemble into HEX packed micelles from selective solvents . Moreover, molecules containing discoid moieties can self-assemble into highly ordered structures due to the p–p stacking. In fact, in order to create ordered self-assemblies, hydrogen bonding, electrostatic attraction, complex effects, or even p–p stacking, etc. can work to make ordered supra-molecules which may tend to further self-organize to form larger well-defined supra-structures. Therefore, to create order in self-assembled materials, it is essential to design molecules with functional moieties that may combine some specific interactions.

It’s known that crown ether-containing compounds can form well-defined structure due to the specific affinity between the crown ether rings . A new kind of two-armed

polymer with a crown ether core (2.30) was designed to create self-assembled structures. By spin coating tetrahydrofuran (THF) solutions of such two-armed polymer onto substrates, macroporous films with disordered arrangement were obtained. A speculated assembly mechanism involving the formation of a series of possible mesogens was proposed. Accordingly, the speculated mesogens are likely to randomly frozen upon a shock solvent evaporation induced by spin coating.



(2.30)

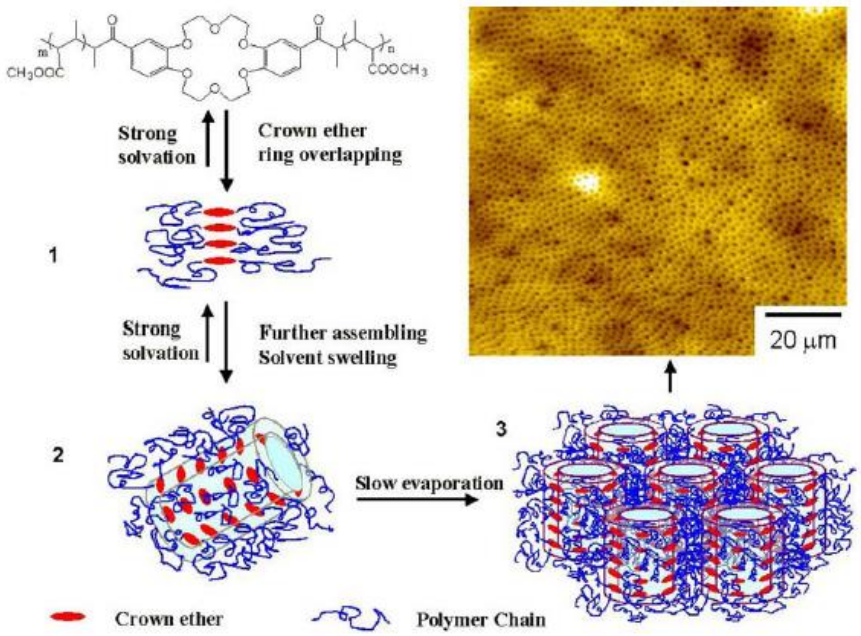
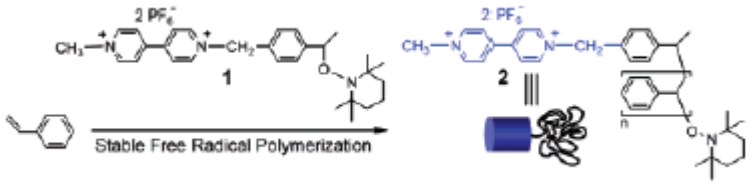


Figure 2.1: Schematic illustration of a proposed self-assembling process and a typical honeycomb-like macroporous film cast from 0.25% THF solution after spontaneous THF evaporation.

2.4.3.2 A Supramolecular Triarm Star Polymer from a Homotropic Tris(Crown Ether) [66]

The construction of analogues of traditional macromolecules by supramolecular methods is a topic of great current interest due to not only their topological importance but also their potential

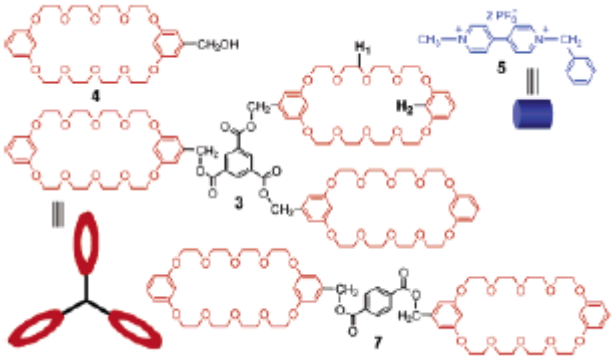
functions. Recent examples include dendrimers from cooperative complexation of a homotritopic guest and complementary monotopic dendron hosts, supramolecular modification of dendrimers, a hyperbranched polymer from self-assembly of an AB_2 monomer, and linear polymers from self-organization of well-defined building blocks. Covalent star polymers have been widely studied. General methods of preparing them are living polymerizations with multifunctional initiators, coupling reactions of macromolecular chains with multifunctional cores, and polymerizations of difunctional monomers with living polymer precursors as initiators. The preparation of the first supramolecular star polymer based on pseudorotaxane complexation. It is from self-assembly of a homotritopic tris(crown ether) host and a complementary monotopic paraquat-terminated polystyrene guest based on the bis(*m*-phyenylene)-32-crown-10/paraquat recognition motif by a supramolecular coupling method, a new method for fabrication of star polymers by using nonconvalent interactions. The strategy we used to introduce a paraquat moiety at the end of every polystyrene chain is to utilize paraquat-functionalized initiator **1** in the stable free radical polymerization of styrene.



(2.31)

The homotritopic core molecule, **3**, was prepared by the reaction of monofunctional crown ether **4** and 1,3,5-benzenetricarbonyl trichloride. Chloroform solutions of host **3** and guest polymer **2** are yellow due to charge-transfer interactions between electron-rich crown ether moieties on **3** and the electron-poor paraquat end unit on **2**.

The complex between the homotritopic host **3** and monotopic paraquatterminated polystyrene guest **2** has a 1:3 stoichiometry as demonstrated by a mole ratio plot (Figure 2a). The model system based on **3** and monotopic guest **5** also has a 1:3 stoichiometry (Figure 2b). Therefore, supramolecular triarm star polymer **6** forms from tritopic host **3** and monotopic polymeric guest **2** in solution (2.28)



(2.32)

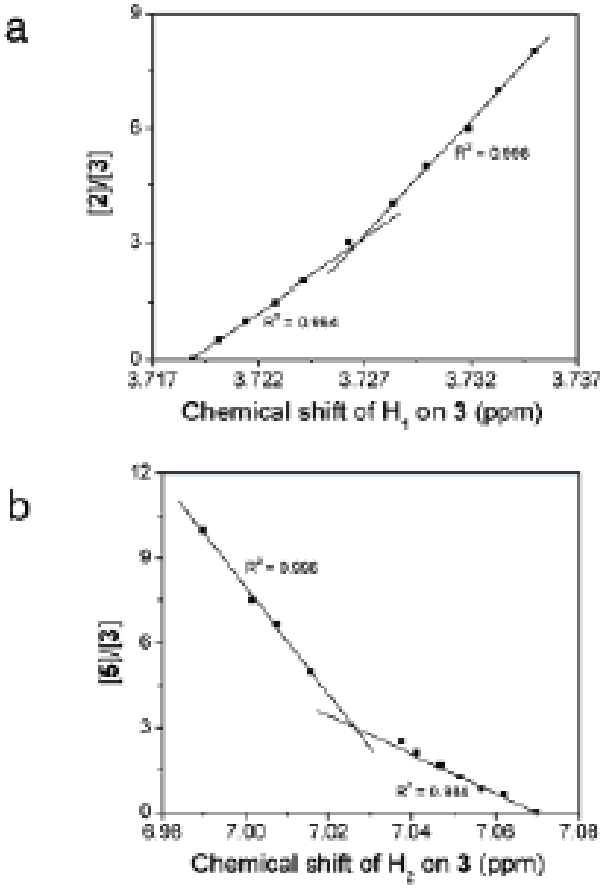
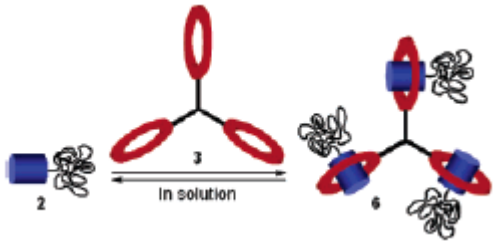


Figure 2.2. (a) Mole ratio plot for **3** and **2**, indicating 1:3 stoichiometry. The solvent is CDCl3. $[\mathbf{3}]_0$ = 0.100 mM. (b) Mole ratio plot for **3** and **5**, indicating 1:3 stoichiometry. The solvent is 2:1 CD3COCD3/CDCl3. $[\mathbf{3}]_0$ =0.100 mM.



(2.33)

Schematic Illustration of the Formation of a Supramolecular Triarm Star Polymer **6** from Homotritopic Host **3** and Monotopic Polymeric Guest **2**

3. EXPERIMENTAL PART

3.1. Materials

Methyl methacrylate (MMA, 99% Aldrich), and styrene (St, 99%Aldrich) were passed through basic alumina column to remove inhibitors and then dried over CaH_2 and distilled under vacuum prior to use. *N*,*N*,*N*',*N*'',*N*''- pentamethyldiethylenetriamine (PMDETA, Aldrich) distilled over NaOH. Tetrahydrofuran (THF, 99.8%, J.T.Baker HPLC grade) was dried and distilled over lithium aluminium hydride. Dichloromethane was purchased from Aldrich and used after distillation over P_2O_5. 4-dimethylamino pyridinium-4-toluene sulfonate (DPTS) was prepared according to the literature procedure [51]. 2,2-bis(hydroxymethyl)propanoic acid (bis-MPA, 99% Across), triethylamine (Et_3N, 99% Merck), 2-Bromoisobutryl bromide (99% Aldrıch), 4-dimethylaminopyridine (DMAP, 99% Aldrıch), *N*,*N*-dicyclohexylcarbodiimide (DCC, 99% Across), 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, 98% Across), 2,2-dimethoxypropane (98% Across), Benzoyl peroxide (BPO, 77% Fluka), absolute ethanol (99.5% J.T.Baker) were used as received. Potassium picrate was prepared by a reaction of picric acid and potassium hydroxide in aqueous methanol, recrystallized from this solvent mixture and dried under vacuum at 80 ^{o}C. 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1yl oxy)-ethyl ester, **11** was synthesized according to our previously reported procedures [76]. 4'-carboxybenzo-15-crown-5, **10** was synthesized according to the published procedure [68]

3.2. Synthesis of Initiator

3.2.1. Synthesis of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethyl ester [1]

In a 100 mL of two-necked round bottom flask, equipped with a magnetic stirrer, TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) (1.5 g, 9.6 mmol) and BPO (2.3 g, 9.6 mmol) were dissolved in 30 mL of freshly distilled Styrene, then flask conducted three times evacuation and subsequent argon purging. The solution was kept for 30 minutes stirring at 90 ^{o}C in an oil bath. After that period more styrene removed via back distillation and flask dissolved in 100 mL of ethyl acetate then extracted two portions (50 mL) of NaOH (1%). The combined organic phase was dried with Na_2SO_4 and solvent evaporated. The crude product purified by column chromatography over silica gel eluting just with dichloromethane, and the product fully purified by recrystallization from cold methanol concentrated to yield 1.43 g (3.75 mmol, 40%) as white needles.

3.2.2. Synthesis of 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethanol [2]

Product **1** (2.4g, 6.3 mmol) was dissolved in 35 mL of absolute ethanol and 8.5 mL of 0.2 N KOH and kept for 5 h to reflux. After the product is extracted with water and dichloromethane (1:1). The combined liquid phase is again extracted with dichloromethane and combined organic phase dried with Na_2SO_4, evaporation of the solvent yielded 1.65 g (5.95 mmol, 95%) as yellow viscous liquid without further purification.

3.2.3. Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid [3]

The 2,2-bis(hydroxymethyl)propanoic acid (4 g, 29.84 mmol) along with *p*-TSA (0.112, 0.58 mmol), and 2,2-dimethoxypropane (5.6 mL, 44.8 mmol) dissolved in 20 mL of dry acetone , and stirred 2 h at room temperature. In the vicinity of 2 h, while stirring continued the reaction mixture was neutralized with 3 mL of totally NH_4OH (25%), and absolute ethanol (1:1), filtered off by-products and subsequent dilution with dichloromethane (50 mL) , and once extracted with distilled water (20 mL). The organic phase dried with Na_2SO_4, concantrated to yield 3.7 g (21.2 mmol, 71%) as white solid after evaporation of the solvent.

3.2.4. Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6-trimethyl-piperidin-1-yloxy)-ethyl ester [4]

Compound **2** (1.634 g, 5.89 mmol) was dissolved in 10 mL of dry dichloromethane along with compound **3** (1.077 g, 6.19 mmol), and DPTS (0.275 g, 0.88 mmol) were added in that order, after stirring 5 minutes at room temperature DCC (1.57 g, 7.613 mmol) dissolved in 5 mL CH_2Cl_2 was added. Reaction mixture was then left overnight at room temperature to stir. After filtration off the urea by product, the solvent removed, and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (9:1). To remove any other byproduct after column 10 mL of cold hexane was added, and filtrate off, solvent removed in vacuum to give the yield 1.516 g (3.5 mmol, 60%) as pale yellow.

3.2.5. Synthesis of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester [5]

Compound **4** (1.516 g, 3.5 mmol) was dissolved in 12 mL of THF and 12 mL of 1 M HCl. The reaction mixture was then stirred for 2 h at room temperature. The precipitated product was filtered off, after removing of THF in vacuum, the reaction mixture extracted with 20 mL of CH_2CL_2, and same amount of distilled water. The combined organic phase dried with Na_2SO_4, evaporation of the solvent concentrated to yield 1.06 g (2.7 mmol, 77%) as white solid.

3.2.6. Synthesis of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester [6]

Compound **5** (1.06 g, 2.7 mmol) was dissolved in 10 mL of CH_2CL_2, and Et_3N (1 mL, 5.94 mmol) was added. The reaction mixture was cooled to 0 ^oC. 2-Bromoisobutryl bromide was added dropwise within 30 minutes. The reaction mixture was stirred 4 h at room temperature. After filtration off little byproduct, the mixture extracted with CH_2CL_2, and saturated aq. $NaHCO_3$. The water phase again extracted with CH_2CL_2, and combined organic phase dried with Na_2SO_4. The solution was concentrated, and the crude product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (10:1) to give the yield 0.73 g (1.35 mmol, %50) as pale yellow.

3.2.7 Synthesis of 1,11-dichloro-3,6,9-trioxaundecane [7]

A mixture of 86 g (0.44 moles) of tetraethylene glycol, 400 ml of benzene, and 77,2 g (0.98 moles) of pyridine was heated to 86 ^{0}C (reflux), and 116 g (0.98 moles) of thionyl chloride was added dropwise with stirring in 3 hr. During this period the reflux temperature of the mixture dropped from 86 ^{0}C to 78 ^{0}C, and a white precipitate was formed. Heating was continued overnight (16 hr) and, after cooling, 10 ml of concentrated hydrochloric acid diluted with 40 ml of water was added dropwise in about 15 min. Benzene was removed from the upper layer containing the product, and the residue (94.6 g) was distilled from a rotary evaporator at about 95 ^{0}C. The product, a light yellow liquid, weighed 93.8g (yield, 92 %)

3.2.8 Preparation of 2,3-Benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene [8]

A mixture of 27.5 g (0.25 mole) of catechol, 375 ml of 1-butanol, and 21.25 g (0.53 moles) of sodium hydroxide dissolved in 25 ml of water was stirred for 5 min under nitrogen and treated with 57.75 g (0.25 mole) of 1,11-dichloro-3,6,9-trioxaundecane. The mixture was refluxed with good agitation for 30 hr during which time the temperature dropped from 102 to 100 ^{0}C. The mixture was acidified with 8 ml of concentrated hydrochloric acid, cooled to 30 ^{0}C, and filtered, and the solids were washed with 100 ml of methanol. The filtrate and the washings were combined and evaporated to dryness in a rotary vacuum evaporator. The residue weighing 72.25 g was extracted continuously with n-heptane at 80-90 ^{0}C for about 3 hr and gave 43.25 g of white flakes containing 95 % of the desired compound, yield 62 %. Analytically pure compound was obtained by recrystallizing from n-heptane.

3.2.9 Synthesis of 4'-Acetobenzo-15-Crown-5 [9]

Into a beaker 500 ml with mechanical stir, polyphosphoric acid (PPA, 100 ml), 12.5 ml of acetic acid, and 4 ml of acetic anhydrate were added. After heated up to 45 ^{0}C, benzo-15-crown-5 (10 g, 0.37 mmol) was dissolved into 15 ml of acetic acid and then it was added dropwise within 1 h into solution. The mixture was reacted under 45 ^{0}C under stirring for 3 h. After cooling to room temperature, 125 ml of distilled water and 125 ml of ice were dropped slowly with stirring to decompose PPA. After completion of addition, the mixture was further stirring for additional 30 min, and then extracted by chloroform (4x50 ml). The combined extracted were washed with saturated sodium carbonate two times, and the distilled water until neutralization, dried over anhydrous sodium sulfate. After solvent was evaporated under

reduced pressure, the yellow oil product was obtained. After crystallization four times from n-heptane, a white product was obtained in 58 % yield.

3.2.10 Synthesis of 2,3-(4'-Carboxybenzo)- 1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4'-Carboxybenzo-15-Crown-5 [10]

To a stirred solution of 4.4 g (110 mmol) of sodium hydroxide in 30 ml of water at 0-10 ^{0}C was added dropwise 1.4 ml (27.6 mmol) of bromine. To this mixture, 2.1 g (66 mmol) of 4'-acetobenzo-15-Crown-5 (for the synthesis of this compound, see ref 5) was added portion wise in 15 min with vigorous stirring. The temperature, which initially increased to 40 ^{0}C, was maintained at 20 ^{0}C with an ice bath. After 5 hr, 0,832 g (8 mmol) of sodium bisulfate was added to destroy excess sodium hypobromide. The reaction mixture was filtered, then extracted with chloroform to remove any unreacted ketone. The aqueous layer was acidified with concentrated HCI to precipitate the acid. After cooling to 0-5 ^{0}C the solution was filtered and the white precipitate washed with distilled water. Recrystallization from ethanol afforded 1,9 (92 %) of pure 4'-Carboxybenzo-15-Crown-5: mp 180 ^{0}C.

3.2.11 Synthesis of 6, 7, 9, 10, 12, 13, 15, 16 – octahydro - 5, 8, 11, 14, 17 -pentaoxa-benzocyclopentadecene-2-carboxylic acid 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl ester [11]

Compound **6** (0.868 g, 1.60mmol) was dissolved in 10 ml of dry dichloromethane along with compound 4'-Carboxybenzo-15-Crown-5 (0.59g, 1.92 mmol), DMAP (0.023g, 0.192 mmol), and DPTS (0.085g 0.273 mmol) were added in that order, after stirring 5 minutes at room temperature DCC (0.49g , 2.4 mmol) dissolved in 5 ml CH_2Cl_2 was added. Reaction mixture was then left overnight at room temperature to stir. It was filtered, evaporated and the remaining product was purified by column chromatography over silica gel eluting once with hexane / ethylacetate (4:1) to remove unreacted **6**, and then with ethylacetate to give **11** as viscous colorless liquid (Yield: 0.85 g, 64 %).

3.3 Synthesis of Polymethylmethacrylate (PMMA) Macroinitiator [12]

PMMA macroinitiator was prepared by ATRP of MMA using **11** as an initiator and copper chloride (CuCl) complexed by *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as the catalyst in toluene (MMA/toluene = 1; v/v) at 60 ^{o}C. To a Schlenk tube equipped with a magnetic stirring bar, the degassed MMA, (3.1 mL, 29 mmol), ligand, (PMDETA, 0.030 mL, 0.145 mmol), CuCl (0.014 g, 0.145 mmol) and initiator (0.12 g, 0.145 mmol) were added in the order mentioned. The tube was degassed by three freeze-pump-thaw cycles, left *in vacuo*

and placed in a thermostated oil bath at 60 ^{o}C for 40 min. Subsequently the polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in a vacuum oven at 25 ^{o}C. The isolated PMMA macroinitiator **12** had the predicted molecular weight and low polydispersity ($M_{n,GPC}$ = 5800 , M_w/M_n= 1.20). $[M]_o/[I]_o$ = 200; conv. =13 %; $M_{n,theo}$ = 3450; $M_{n,NMR}$ = 5700

3.4 Synthesis of PMMA-*b*-PS Block Copolymer [13]

PMMA-*b*-PSt block copolymer was prepared using NMP of St (0.731 mL, 6.4 mmol) in the presence of TEMPO functionalized PMMA as a macroinitiator, (0.182 g, 0.032 mmol). The reaction mixture was degassed by three freze-pump-thaw cycles and left in *vacuo*. The tube was then placed in an oil bath thermostated at 125 ^{o}C for 15 h. The polymerization mixture was diluted with THF, and precipitated in methanol. The obtained block copolymer was dried for 24 h in a vacuum oven at 25 ^{o}C. $[M]_o/[I]_o$ = 200; conv. 34 %; $M_{n,theo}$ = 12800; $M_{n,GPC}$ = 12500 ; M_w/M_n = 1.22; $M_{n,NMR}$ = 12800

3.5 Preparation of Potassium Picrate

Potassium picrate was obtained by neutralizing picric acid with the KOH in aqueous MeOH, recrystallization of the salt form this solvent mixture, and drying the crystalline compound for several days under vacuum at about 80 ^{0}C

3.6 Switching from block to miktoarm star copolymer via cation binding ability of crown ether unit

PMMA-*b*-PSt block copolymer (0.182 gr, 1.42x 10^{-5} mol) was dissolved in 25 ml of dry dichloromethane. Potassium picrate(0.0188 gr, 7x 10^{-5} mol) was dissolved in 25 ml of distilled water. Subsequently, two solution were mixed with good agitation for 3 hr at the room temperature. After that time, potassium picrate didn't pass through organic phase. Decreasing the amount of potassium picrate in water phase was followed with UV spectra. We found that concentration of potassium in dichloromethane was 2.21x10^{-4} M.

3.7 Characterization

The ^{1}H-NMR spectra was recorded on a Bruker spectrometer (250 MHz for proton) in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standart. Gel Permeation Chromatography (GPC) measurements were carried out with an Agilent Model 1100 instrument consists of pump, refractive index dedector, UV dedectors and four Waters Styragel columns (HR 5E, HR 4E, HR 3 and HR 2). THF was used as eluent at flow rate of 0.3 mL/min. at 30 ^{o}C. The molecular weights of the polymers were calculated with the aid of

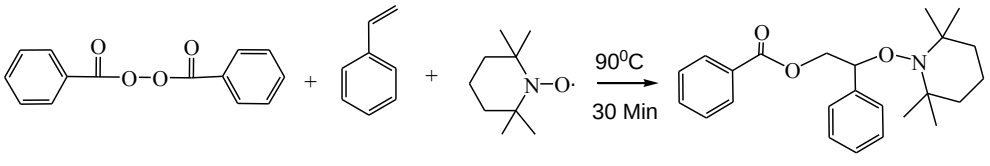
polystyrene standarts (Polymer Laboratories). All polymers obtained were dried overnight under vacuum and the conversions were determined by gravimetrically.

4. RESULTS and DISCUSSION

4.1. Synthesis of Initiator

4.1.1 Synthesis of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester

The initiator synthesis was carried out using Hawker and Hedrick processes [1, 52]. First of all, the synthesis of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (**1**) was carried out by heating styrene in the presence of benzoyl peroxide and TEMPO for 30 minutes. The hydrolysis of ester was then carried out to give the 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperidin-1-yloxy)-ethanol (**2**). The characteristic peak of aromatic protons adjacent to ester group at δ 7.9 ppm completely disappeared after hydrolysis. Moreover, the new signals appeared at δ 5.9 ppm of –OH and the shifts of the $–CH_2$ and –CH protons adjacent to hydroxyl and aromatic group, respectively, clearly confirm the successful hydrolysis. The ^1H NMR spectra of the corresponding ester and alcohol precursors are presented in Figures 2 and 3, respectively.



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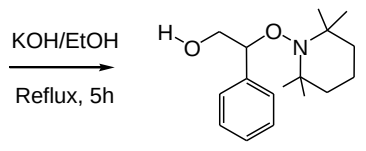

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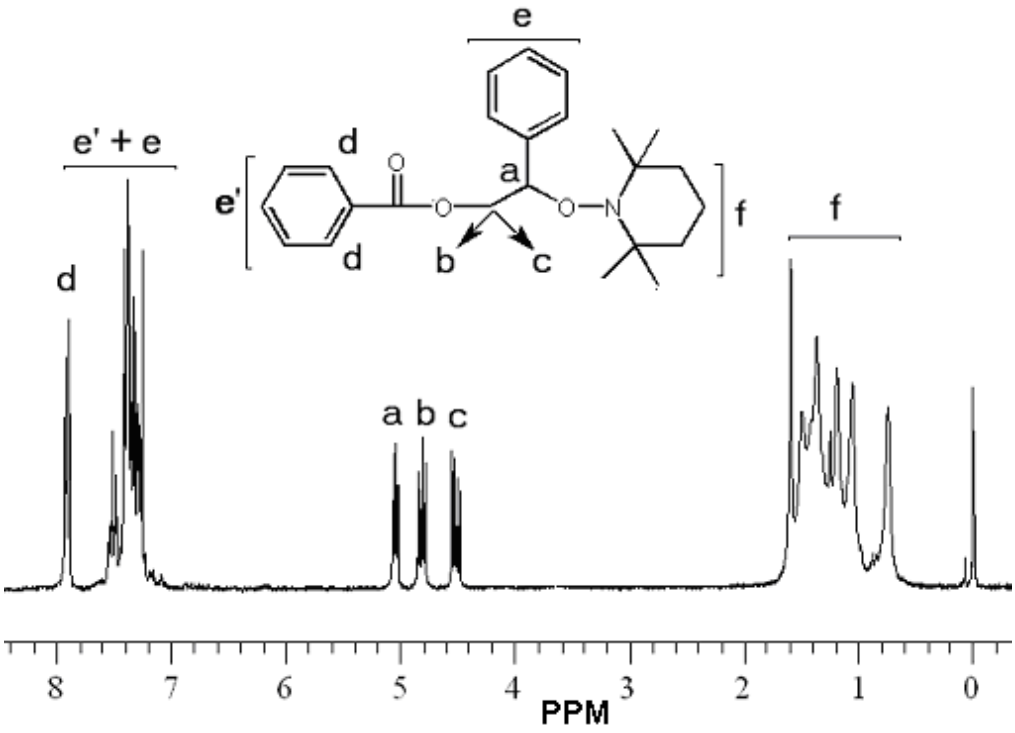


Figure 4.3. The ^{1}H NMR spectrum of benzoic acid 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethyl in $CDCI_3$

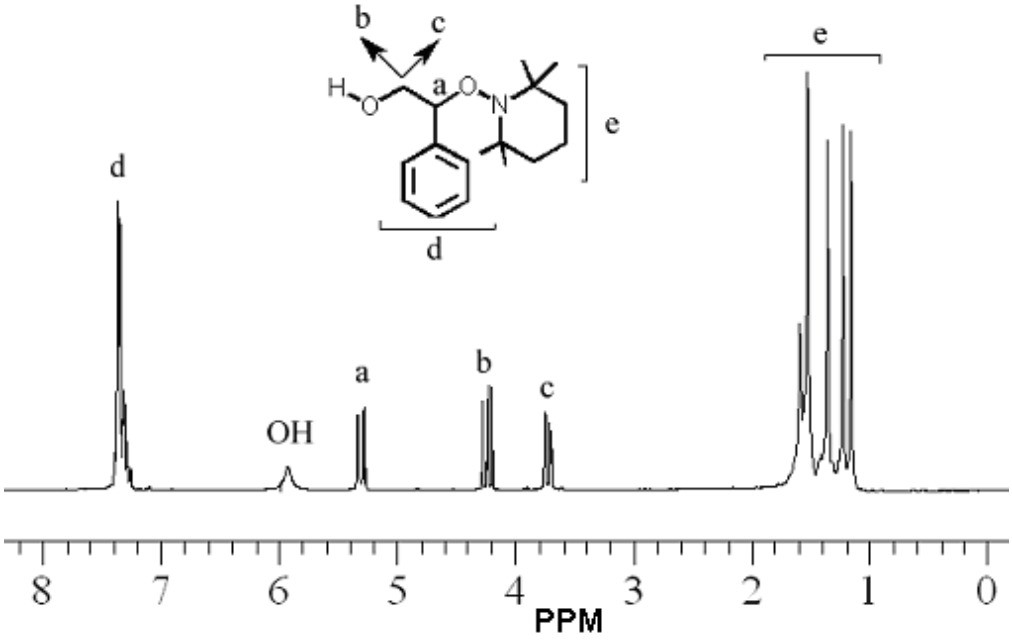
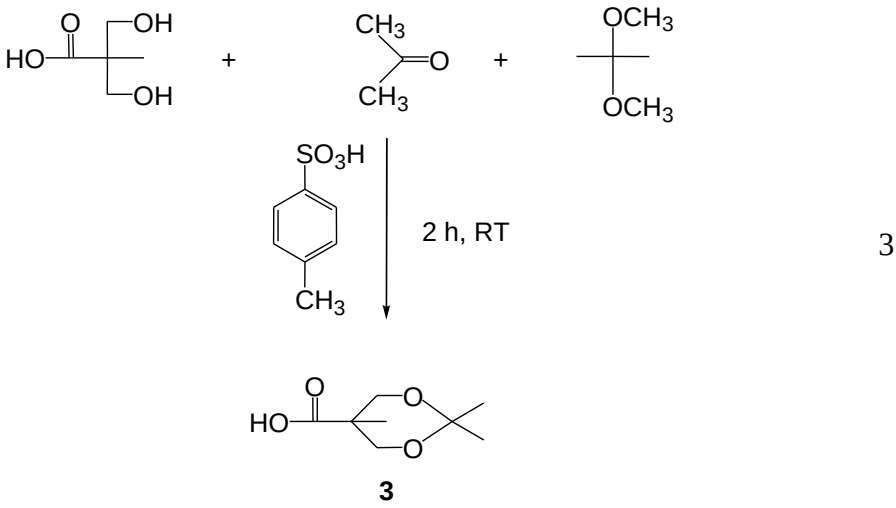


Figure 4.4. The ^{1}H NMR spectrum of 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethanol in $CDCI_3$

In order to convert the hydroxyl functionality at compound **2** into two hydroxyl functionalities, successive protection, esterification and deprotection reactions were realized. For this purpose, the hydroxyl protected acidic compound, **3**, was synthesized according to the following reaction.

In this reaction, 2, 2-bis (hydroxymethyl)-propanoic acid was reacted with excess amount of dry acetone using *p*-toluene sulfonic acid as catalyst. Additionally, 2,2-dimethoxy-propane was deliberately used to provide acetone during the reaction. The ^{1}H NMR spectrum of the compound, (**3)**, is shown in Figure 4.



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3

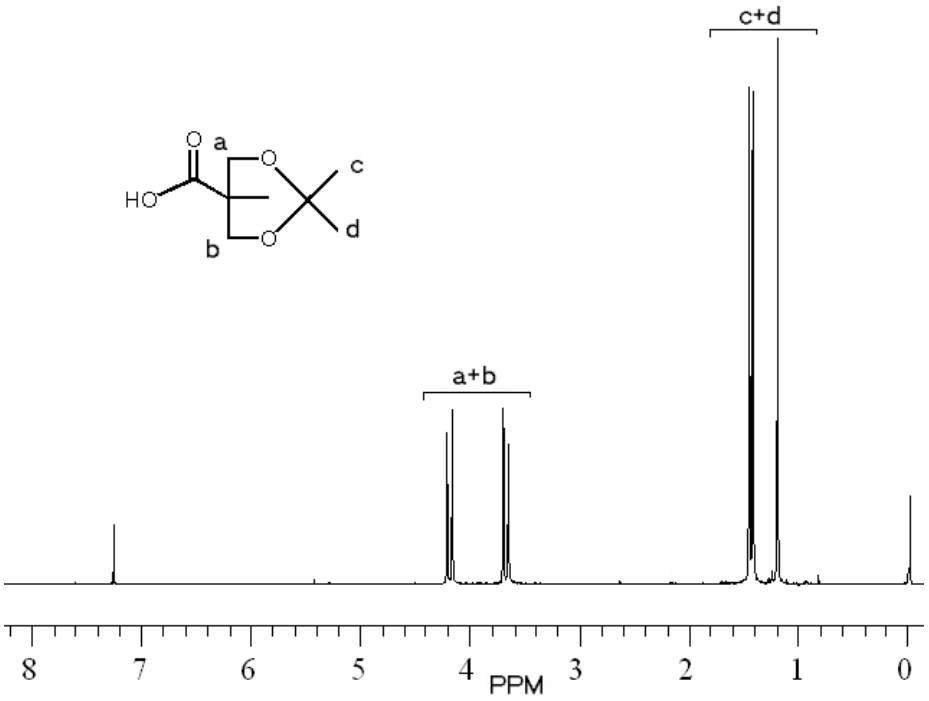
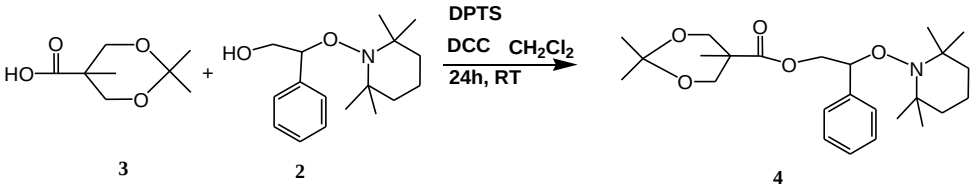


Figure 4.5. The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid in $CDCI_3$

Subsequent esterification reaction between alcohol and hydroxyl protected acid was carried out using catalytic amount of DPTS (dimethylamino-4-toluene-sulfonate). Although this procedure was reported to be a suitable method for the esterification reaction [53], the main drawback of this system is related to the difficulties arising from the removal of formed urea by product. However, this was overcomed by further precipitation followed by filtration method. The ^{1}H NMR spectrum of the compound, (**4),** is shown in Figure 5.



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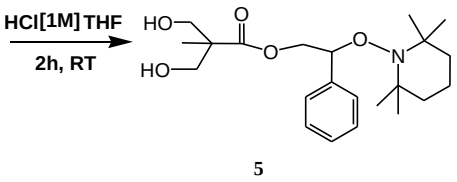

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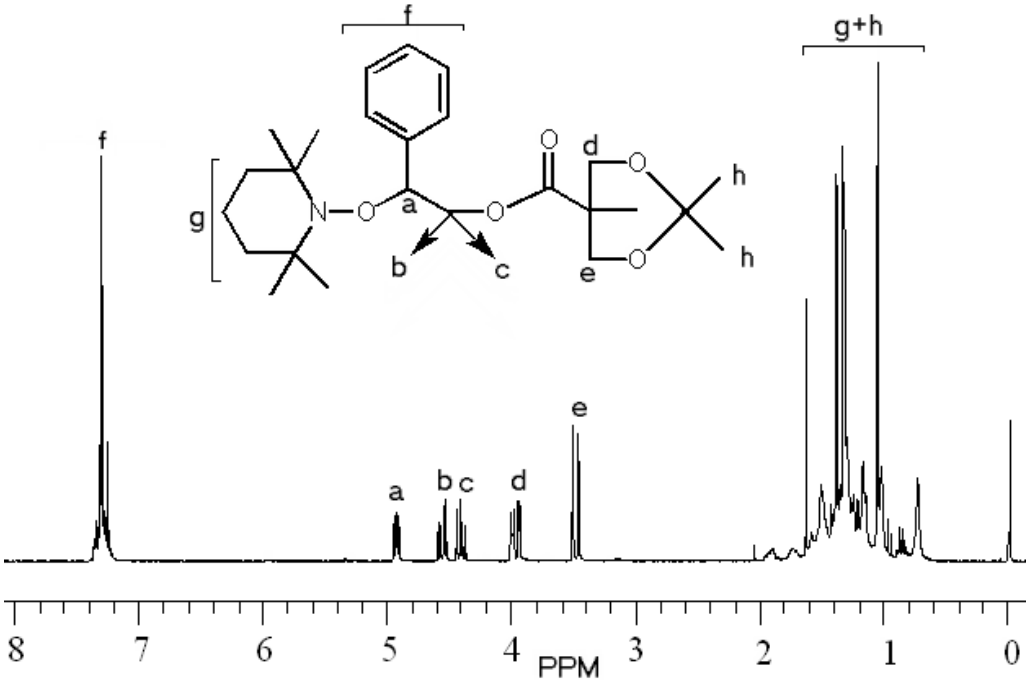


Figure 4.6. The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6-trimethyl-piperidin-1-yloxy)-ethyl ester in $CDCI_3$

Deprotection step was easily achieved by acidic hydrolysis using 1 M HCl and THF at room temperature. ^{1}H NMR spectrum of the desired compound, **(5),** is shown in Figure 6. From the NMR spectrum -OH protons (e-e') at δ 2.7 ppm suggests that deprotection step was carried out successfully.

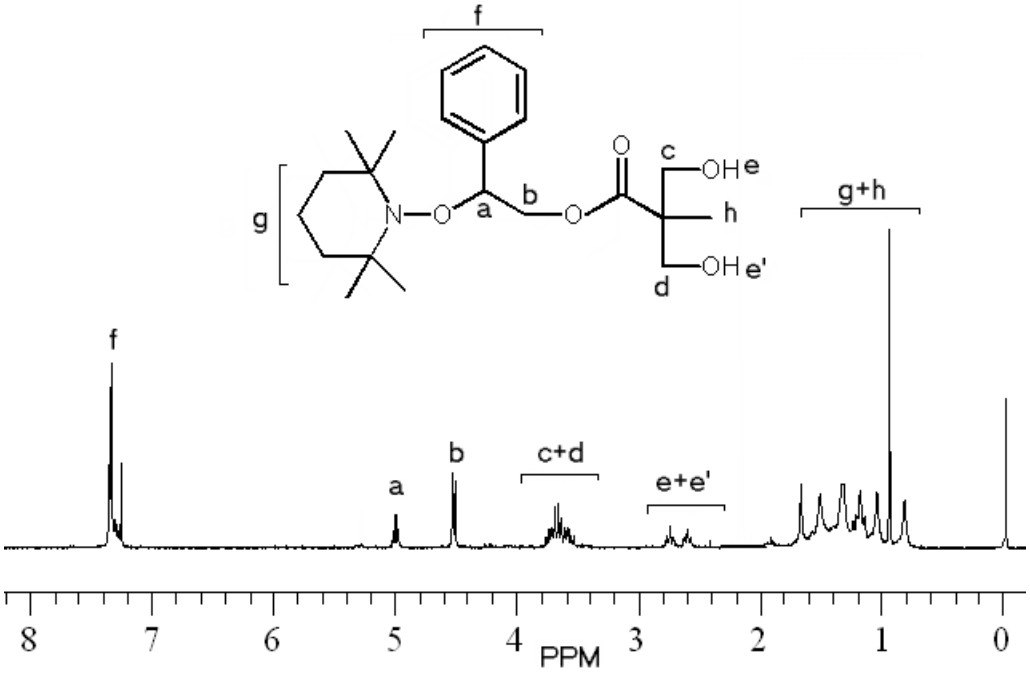


Figure 4.7. The ^{1}H NMR spectrum of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCI_3$

In order to introduce ATRP functionality into the synthesis, second esterification reaction was achieved. In this connection, it should be pointed out that at this step severe reaction conditions may cause the hydrolysis of the ester groups present in the structure. Therefore, the esterification process was performed at 0-5 ^{0}C and 2-bromoisobutryl bromide was added in a dropwise manner. The ^{1}H NMR spectrum of the compound 6 showed that the –OH protons of compound 5 at δ 2.7 ppm completely removed. Moreover, the new –OH proton at δ 2.2 ppm belongs to $–CH_2$ group, the shift of the $-CH_2$ protons adjacent to ATRP functionality to δ 4.1 ppm and the $–CH_3$ protons on ATRP functionality at δ 1.89 ppm indicate that esterification reaction was carried out successfully. The ^{1}H NMR spectrum of the resulting compound, **(6),** is shown in Figure 7.

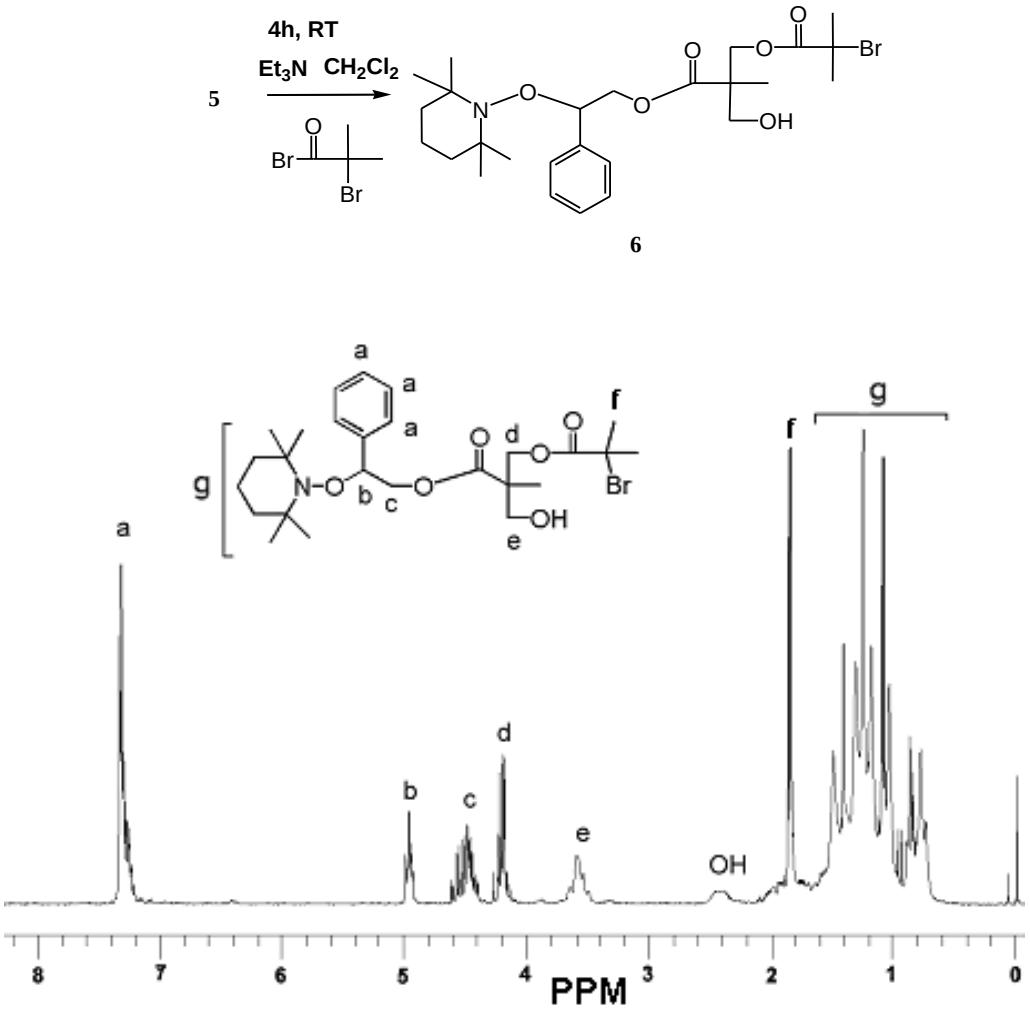


Figure 4.8. The ^{1}H NMR spectrum of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCI_3$

4.1.2. Preparation of 2,3-Benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene [7]

Nucleophilic substitution reaction was carried out between catechol and 1,11-dichloro-3,6,9-trioxaundecane in the presences of aqueous solution of NaOH, and 1-butanol [42]. The mixture was refluxed with good agitation for 30 hr at 100 ^{0}C. After that time, the mixture was acidified with concentrated hydrochloric acid, cooled to 30 ^{0}C and filtered, and the solids were washed with methanol. Pure compound was obtained by recrystallizing from n-heptane. The ^{1}H NMR spectrum of the resulting compound, **(7),** is shown in Figure 9.

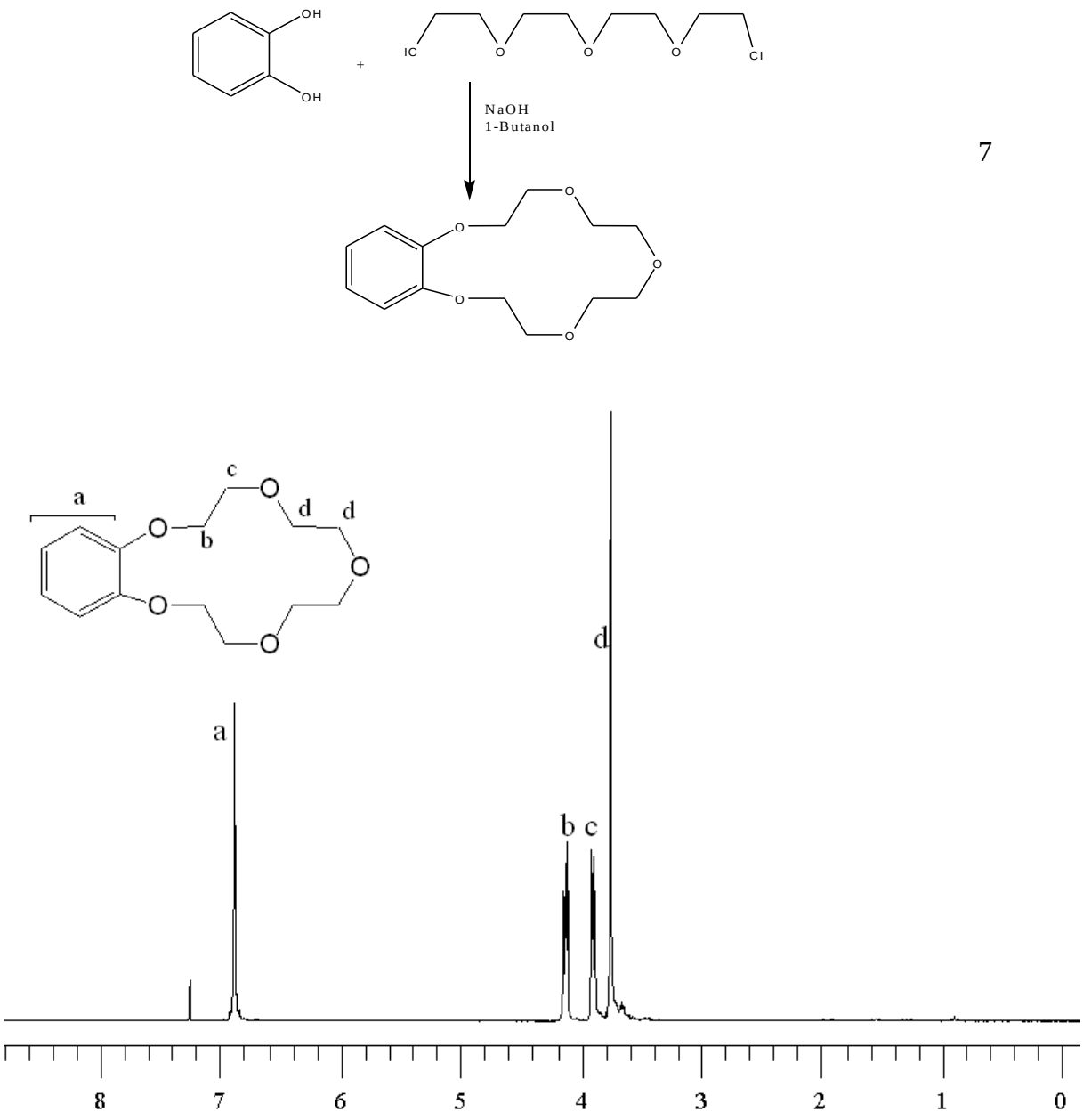
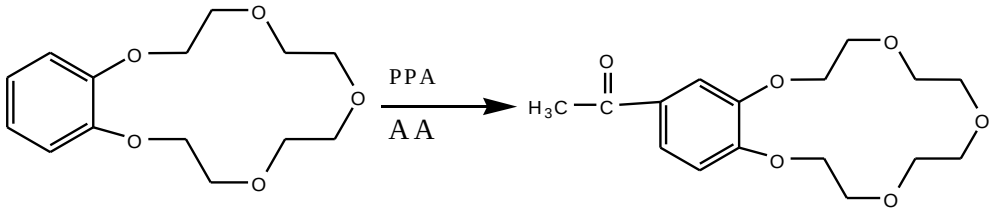


Figure 4.9. The ^{1}H NMR spectrum of Benzo-15-Crown-5 in $CDCI_3$

4.1.3. Synthesis of 4'-Acetobenzo-15-Crown-5 [8]

To obtain compound (8), Benzo-15-Crown-5 and acetic anhydrate (AA) were reacted in the presence of PPA and acetic acid [67]. The mixture was reacted under 45 ^{0}C under stirring for 3 h. After cooling to room temperature, ice-water mixture was added to decompose PPA and then extracted by chloroform. After crystallization four times from n-heptane, a white

product was obtained. The ^{1}H NMR spectrum of the resulting compound, (**8),** is shown in Figure 10.



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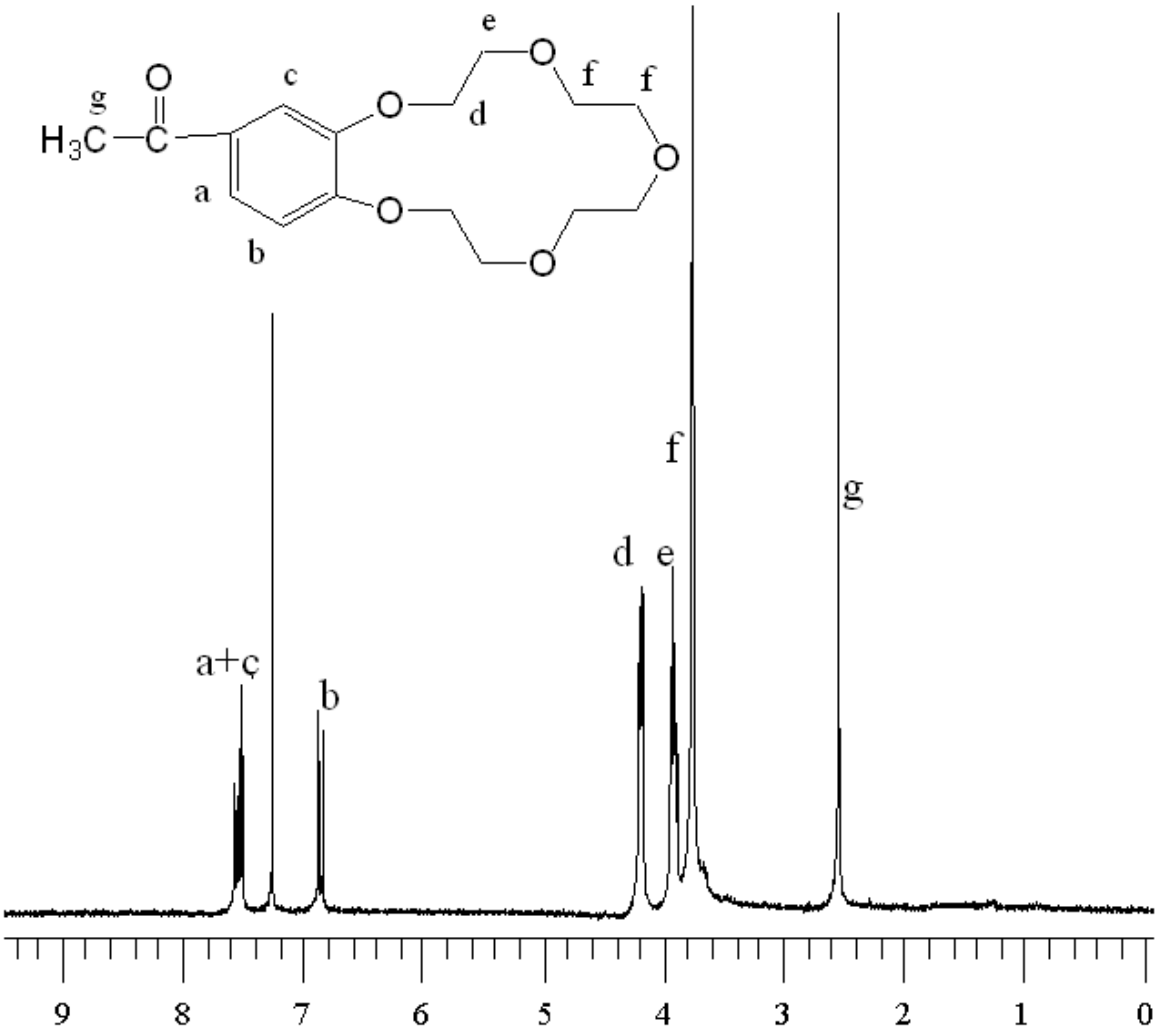
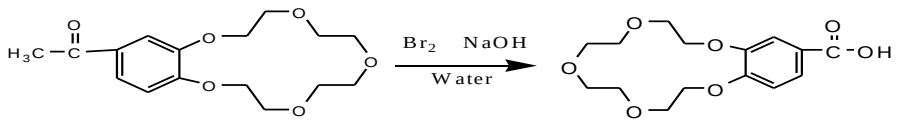


Figure 4.10. The ^{1}H NMR spectrum of 4'-Acetobenzo-15-Crown-5 in $CDCI_3$

4.1.4. Synthesis of 4'-Carboxybenzo-15-Crown-5 [9]

Sodium hypobromide was composed by using solution of NaOH and Br_2. To this mixture, 4'-Acetobenzo-15-Crown-5 was added to form 4'-Carboxybenzo-15-Crown-5 with vigorous stirring at 0-20 ^{0}C with an ice bath [68]. After 5 hr, The reaction mixture was filtered, then extracted with chloroform to remove any unreacted ketone. The aqueous layer was acidified with concentrated HCI to precipitate the acid. After cooling to 0-5 ^{0}C the solution was filtered and the white precipitate washed with water. Recrystallization from ethanol, a white product was obtained. The ^{1}H NMR spectrum of the resulting compound, **(9),** is shown in Figure 11.



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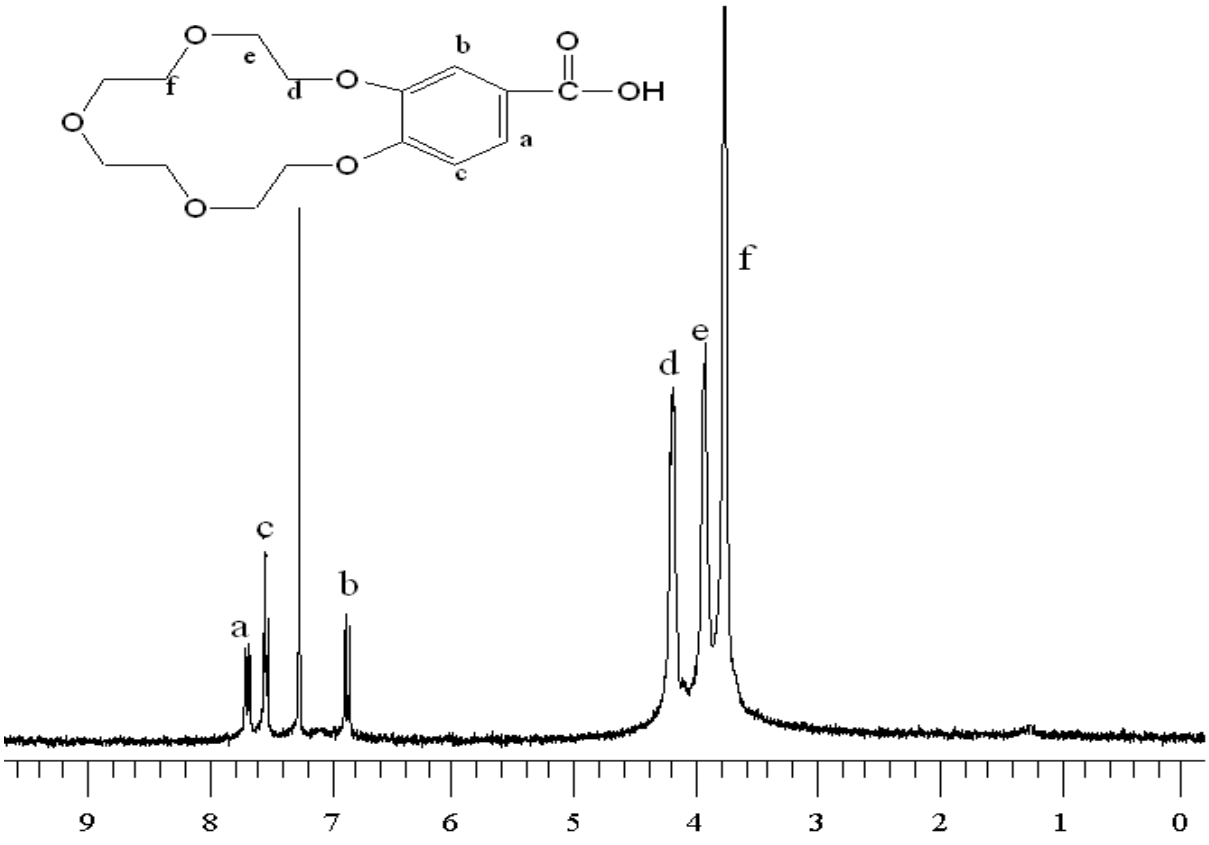
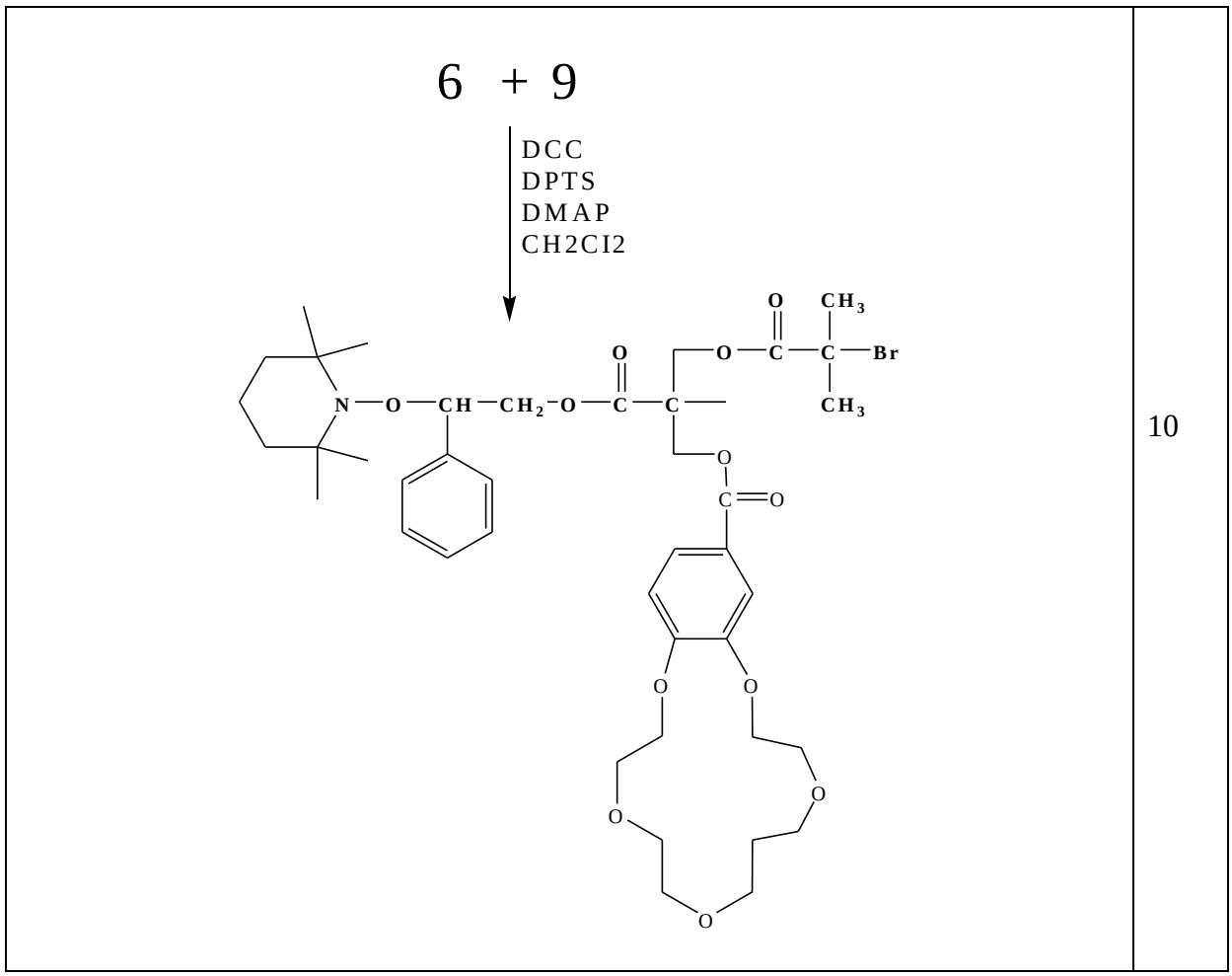


Figure 4.11. The ^{1}H NMR spectrum of 4'-Carboxybenzo-15-Crown-5 in $CDCI_3$

4.1.5. Synthesis of 6, 7, 9, 10, 12, 13, 15, 16 – octahydro - 5, 8, 11, 14, 17 -pentaoxa-benzocyclopentadecene-2-carboxylic acid 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl ester [10]

Third esterification reaction between 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester and 4'-Carboxybenzo-15-Crown-5 was carried out by using catalytic amount of DPTS (dimethylamino-4-toluene-sulfonate), DCC, and DMAP. Although this procedure was reported to be a suitable method for the esterification reaction [53], the main drawback of this system is related to the difficulties arising from the removal of formed urea by product. However, this was overcomed by further precipitation followed by filtration method. Molecular weight of two functional crown initiator was calculated 836gr/mole by theoretically. The characteristic peak of The ^{1}H NMR of the compound, (**10),** were shown in Figure 12 . The molecular weight of synthesized two functional crown ether initiator was proved with TOF MS spectrum which was shown in Figure 13.



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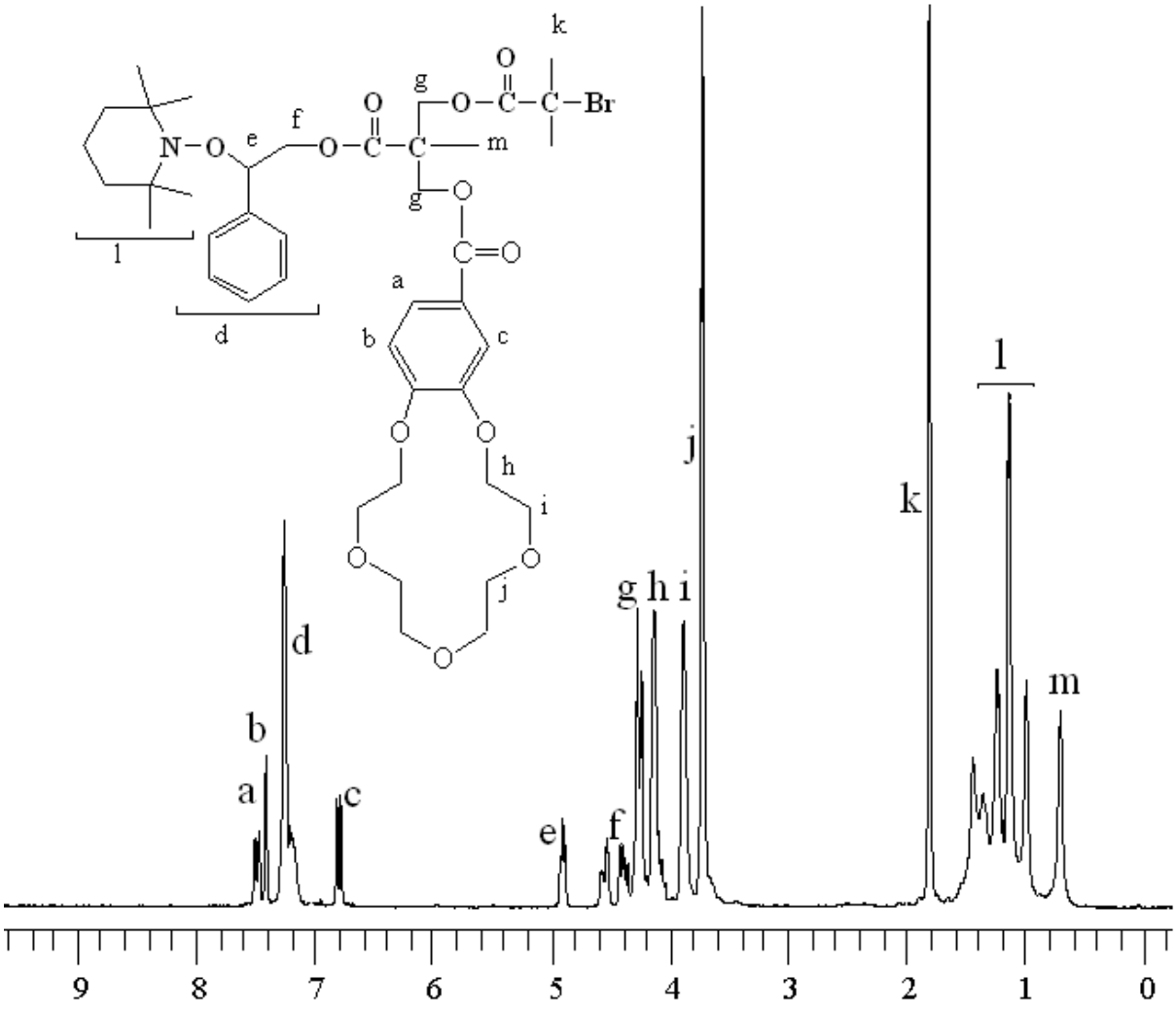


Figure 4.12. The ^{1}H NMR spectrum of 6, 7, 9, 10, 12, 13, 15, 16 – octahydro - 5, 8, 11, 14, 17 -pentaoxa-benzocyclopentadecene-2-carboxylic acid 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl ester in $CDCI_3$

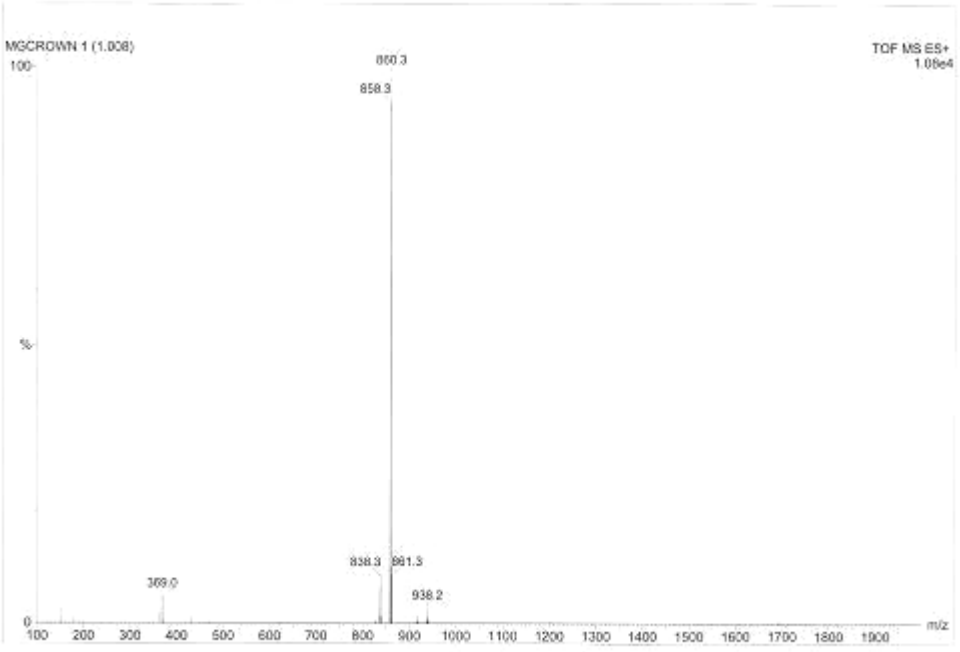
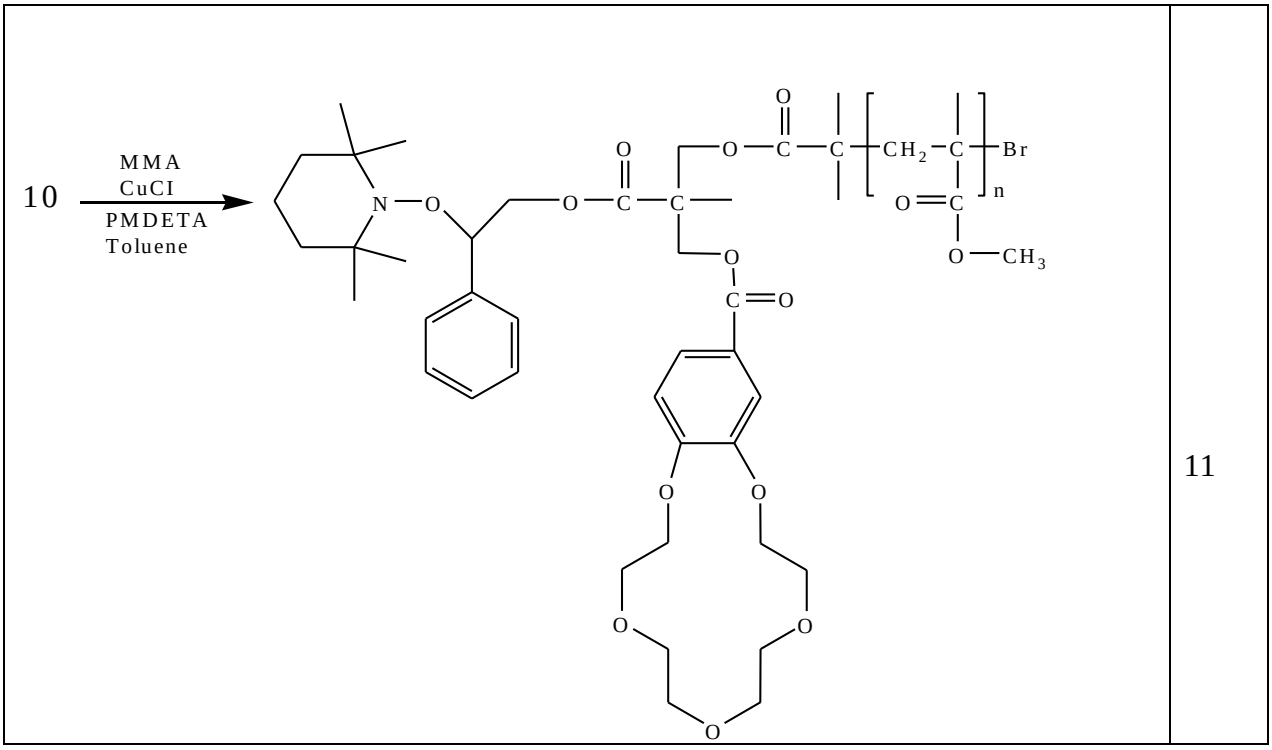


Figure 4.13. The TOF MS spectrum of two functional crown ether initiator

4.2. Synthesis of Polymethyl Methacrylate (PMMA) macroinitiator [11]

Synthesis of polymethyl methacrylate (PMMA) macroinitiator was prepared by ATRP of MMA in a solvent of toluene at 60 ^{o}C using CuCl/PMDETA catalyst system in the presence of crown initiator **10**. The conditions and results are given in Table 4.1. The observed molecular weights of the polymers measured by GPC showed some deviations from those calculated by theoretical and ^{1}H NMR. The reasons of those results can be attributed to the different hydrodynamic volumes of crown ether. The ^{1}H NMR spectra of PMMA macroinitiator is shown in Figure 14. GPC traces of homopolymers and copolymers are shown in Figure 18



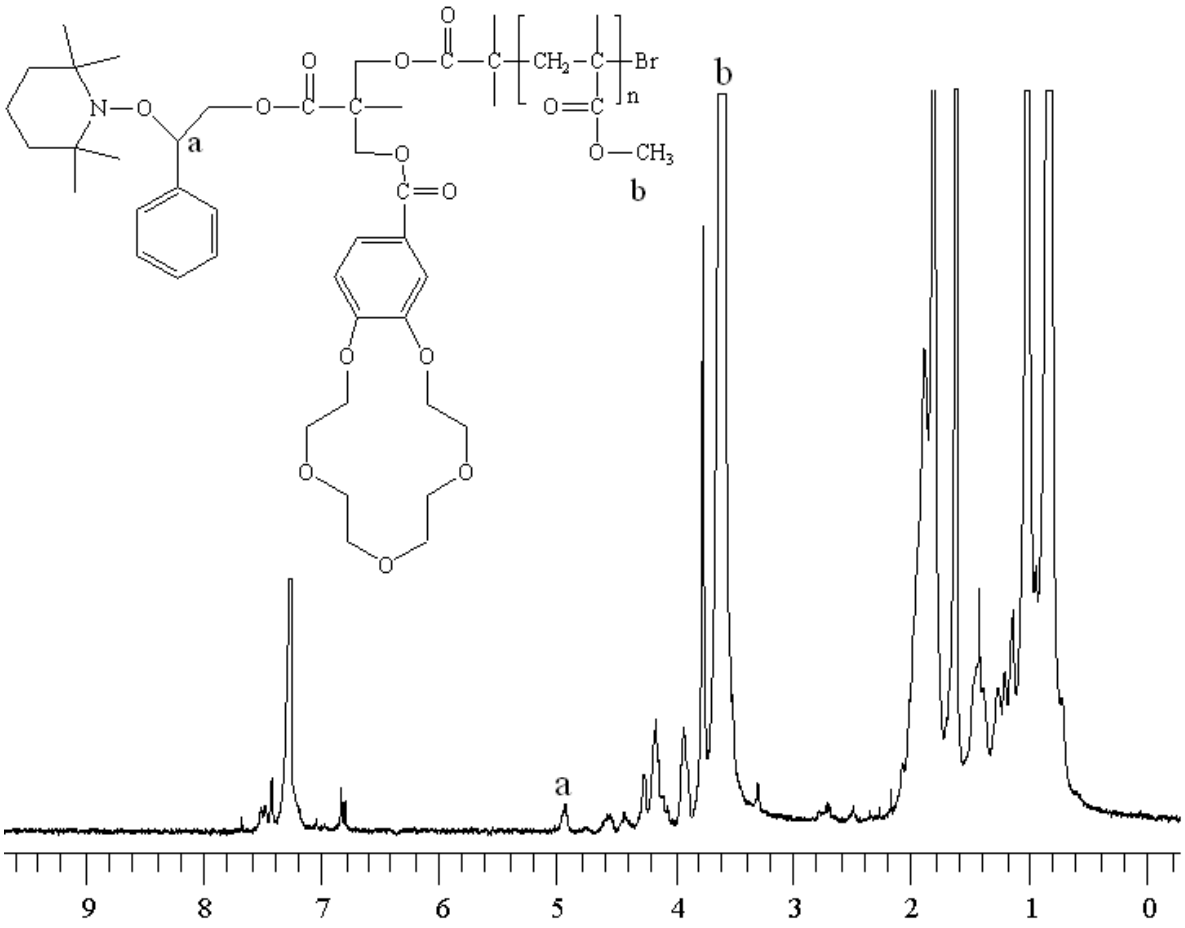


Figure 4.14. The ^{1}H NMR spectrum of polymethyl methacrylate (PMMA) macroinitiato

4.2.1 Kinetic experiment of MMA via ATRP [12]

The plot of ln $[M]_0/[M]$ versus time for PMMA was linear indicating that the rate of polymerization is first order with respect to monomer concentration, which the concentration of radicals was constant throughout the polymerization. The plot of ln $[M]_0/[M]$ versus time for PMMA is shown in Figure 15.

Figure 16 shows how M_n and M_w/M_n varied throughout the polymerization. The experimental number avarege molecular weights of PMMA were determined by GPC based on the linear PMMA standards. The observed molecular weights of the polymers showed some deviations from those calculated by theoretical ones. The reasons of these results can be attributed to the different hydrodynamic volumes of crown ether. According to Figure 15, polydispersity values tend to decrease during the polymerization.

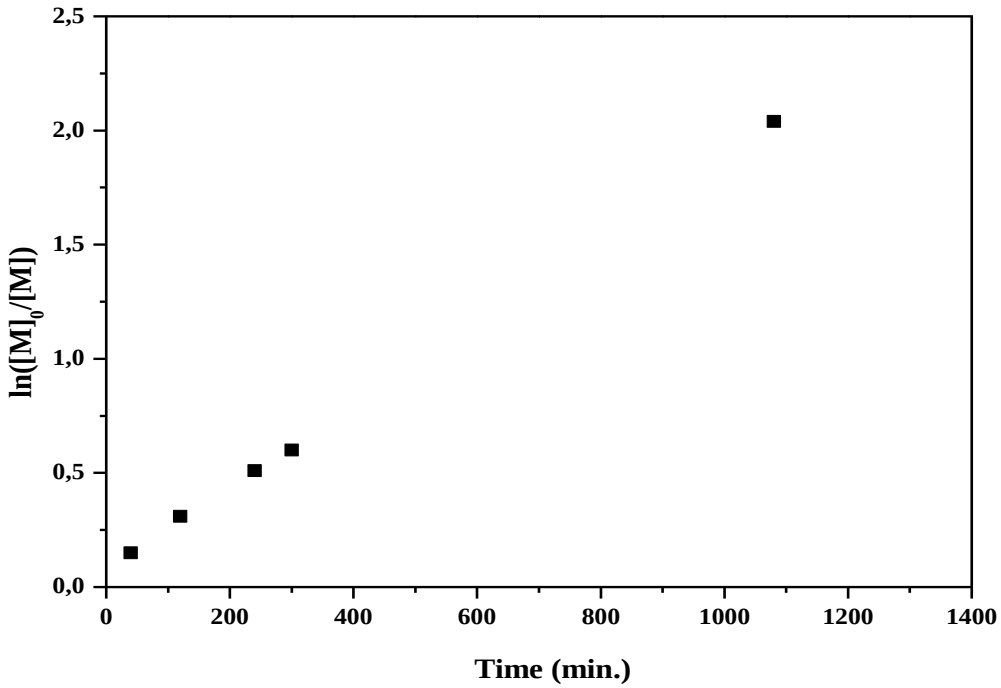


Figure 4.15. The plot of ln $[M]_0/[M]$ versus time for PMMA macroinitiator

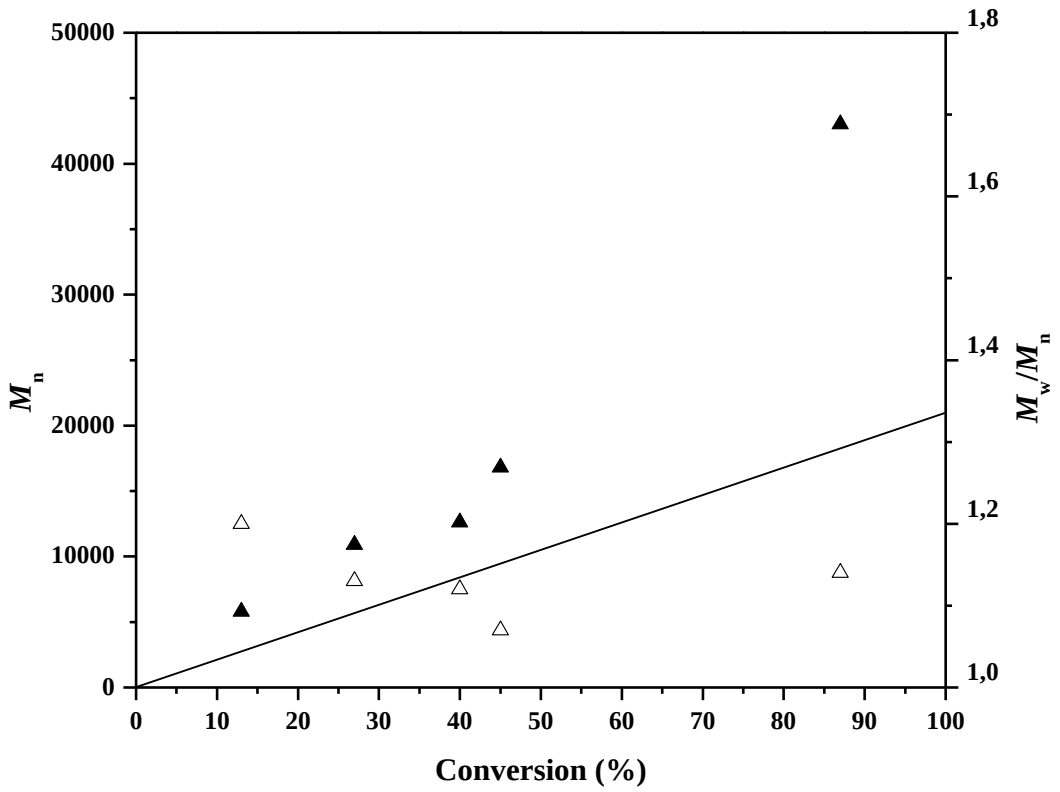
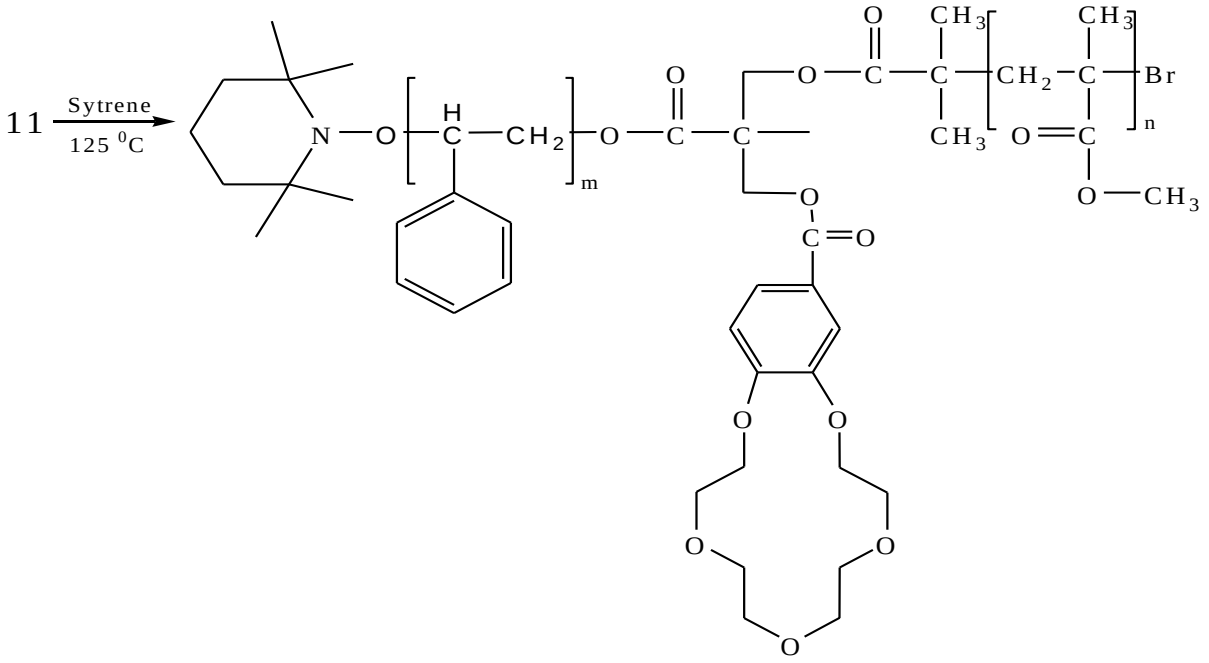


Figure 4.16. Number-average molecular weight and polydispersity as a function of conversion for the solution polymerization of MMA at 60 ºC.

4.3 Synthesis of PMMA-*b*-PS Copolymers [13]

The polymerization reactions were carried out using PMMA as macroinitiator SFRP of styrene (St) in bulk at 125 ^{0}C. The observed molecular weights of PMMA-*b*-PS copolymers determined by GPC were in good agreement with the theoretical ones as can be seen in Table 4.1. The ^{1}H NMR spectrum of PMMA-*b*-PS copolymers the is shown in Figure 17.



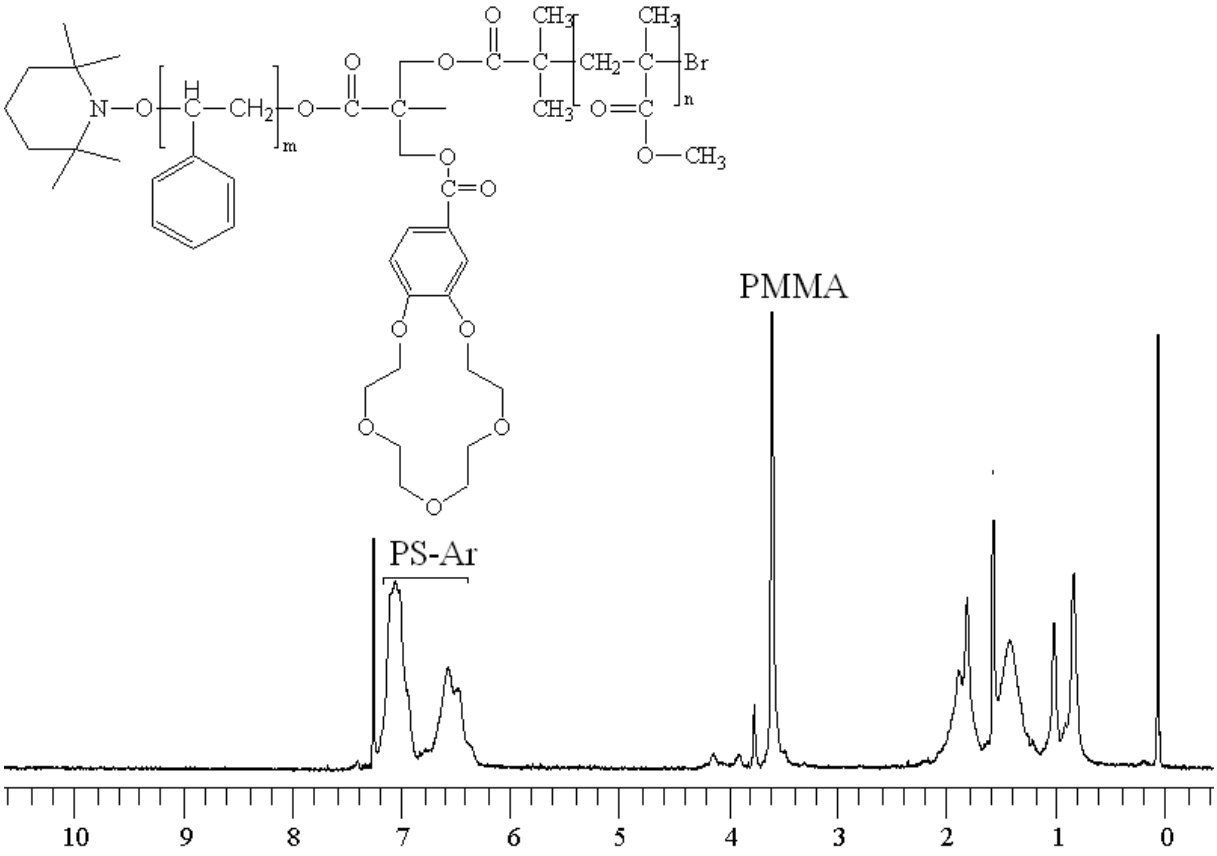


Figure 4.17. The ^{1}H NMR spectrum of PMMA-*b*-PS coplymer

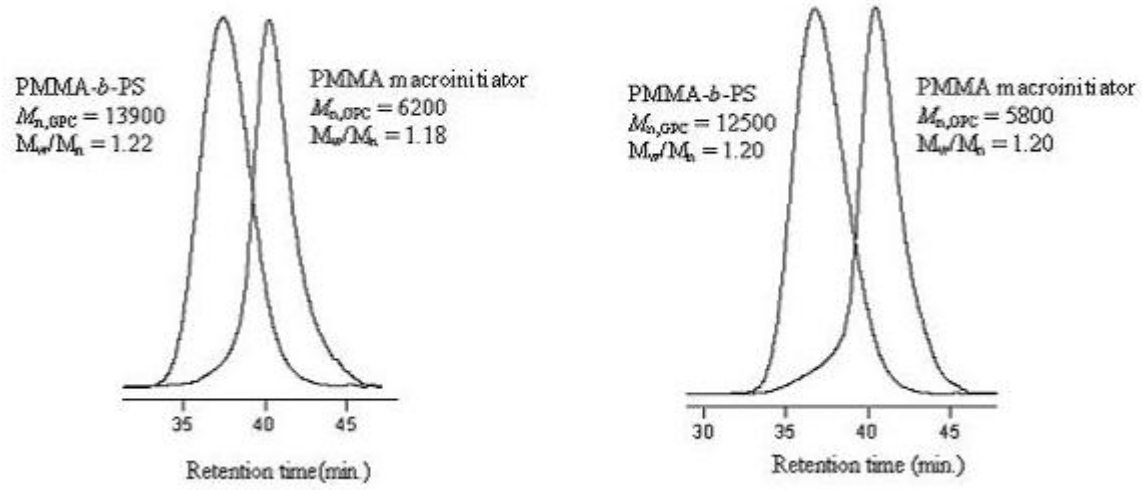


Figure 4.18. The GPC trace of PMMA macroinitiator and PMMA-*b*-PS copolymer

4.4 Switching from block to miktoarm star copolymer via cation binding ability of crown ether unit [14]

Decreasing the amount of potassium picrate in water phase and increasing the amount of potassium picrate in organic phase were followed with UV spectra. The UV spectrums were shown in Figure 19 and 20, respectively. In normal, potassium picrate wasn't dissolved dry dichloromethane. If there is crown ether unit in organic phase, potassium picrate passes on organic phase. We found that crown ether concentration of dry dichloromethane was 2.21×10^{-4}M. The crown to cation ratio was 1.6:1. Assembly of block copolymer into miktoarm star copolymer wasn't synthesized successfully via cation binding ability of crown ether unit by using potassiım picrate.

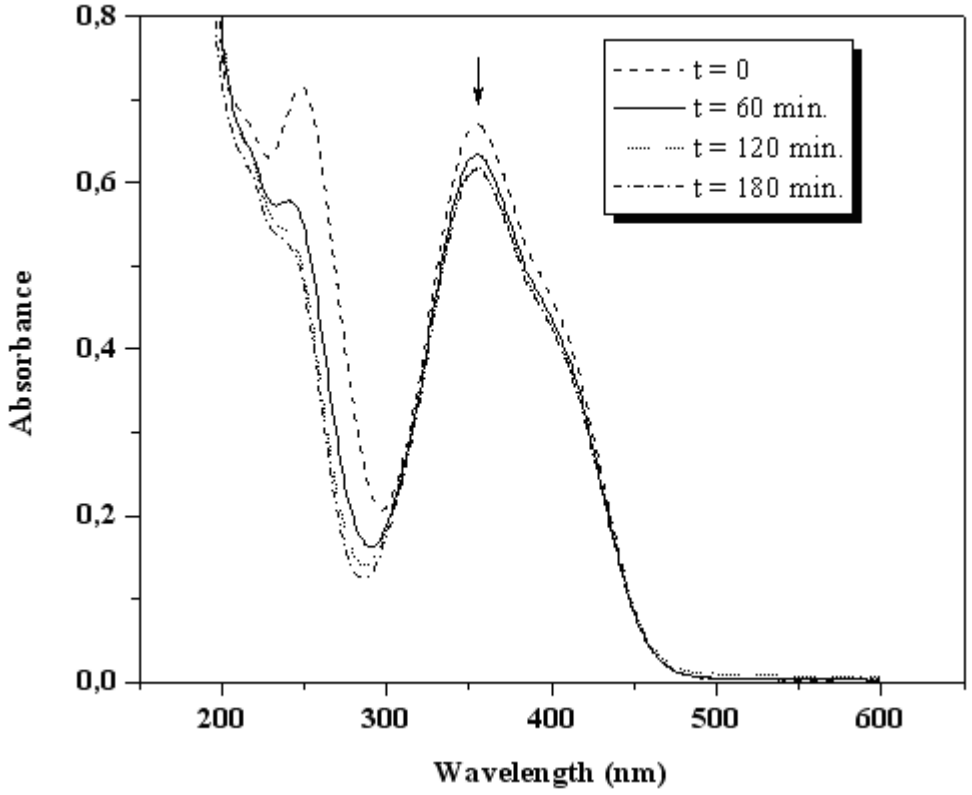


Figure 4.19.The UV spectrum of potassium picrate in water phase

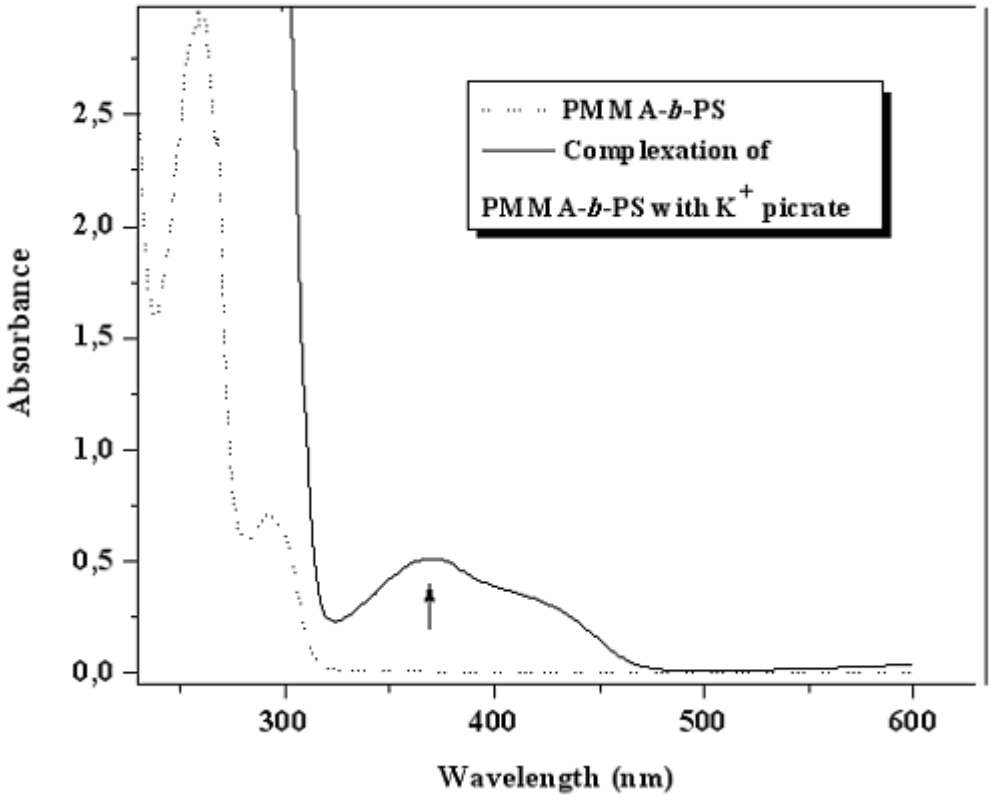


Figure 4.20. The UV spectrum of potassium picrate in organic phase (CH_2CI_2)

Table 4.1. Synthesis of Copolymers via ATRP and SFRP routes

No	Monomer	$[M]_0$ mol.L-1	$[M]_0/[I]_0$	Initiator	Time (min.)	Conv. (%)	$M_{n,theo}$	$M_{n,GPC}$	M_w/M_n	$M_{n,NMR}$[g]
P[1a]	MMA	4.63	100	Crown-initiator	40	30	3900[c]	6200[e]	1.18	5200
P[2a]	MMA	4.65	200	Crown-initiator	40	13	3450[c]	5800[e]	1.20	5700
P[3a]	MMA	4.65	200	Crown-initiator	120	27	6200[c]	8500[e]	1.13	8450
P[4a]	MMA	4.65	200	Crown-initiator	240	40	8800[c]	12600[e]	1.12	12300
P[5a]	MMA	4.65	200	Crown-initiator	300	45	9800[c]	16800[e]	1.07	-
P[6a]	MMA	4.65	200	Crown-initiator	1080	87	17500[c]	43000[e]	1.16	-
P[7b]	St	8.69	200	Macroinitiator[1a]	900	34	12200[d]	13900[f]	1.22	13000
P[8b]	St	8.69	200	Macroinitiator[2a]	900	34	12800[d]	12500[f]	1.20	12800

1a) $[M]_o$: $[I]_0$: $[PMDETA]_0$: $[CuCl]_0$= 100:1:1:1 ; (MMA/Tolouene :1/1)

2a) $[M]_o$: $[I]_0$: $[PMDETA]_0$: $[CuCl]_0$= 200:1:1:1 ; (MMA/Tolouene :1/1)

b) Polymethyl methacrylate (PMMA) macroinitiator

c) $Mn_{,theo} = ([M]_o/[I]_o \times \text{conversion \%} \times (100.12) + \text{MW of initiator}$

d) $Mn_{,theo} = ([M]_o/[I]_o \times \text{conversion \%} \times (104.15) + Mn_{NMR,macroinitiator}$

e) Molecular weights were calculated according to the linear PMMA standards

f) Molecular weights were calculated according to the linear PS standards

g) Molecular weights were calculated according to the PS aromatic protons (5H), MMA (3H) , and two functional crown initiator (1H)

5. CONCLUSION and RECOMMENDATION

In conclusion, to obtain miktoarm star copolymer, the two functional crown ether initiator '**11'** was synthesized after several steps. However, there were still some problems. Especially, separating of the compound '**6'** from the final ester structure due to its higher amount than acid chloride. To remove this impurity, solubility behaviours of the different compounds were investigated. Firstly, the final product was dissolved in a little amount of hexane, removing of the hexane and subsequent vacuum dryness showed that compound '**6'** completly removed from the final ester through ^{1}H-NMR spectrum, but this method led to poor yield (0.04 g %16).

Synthesis of polymethyl methacrylate (PMMA) macroinitiator was prepared by ATRP of MMA in a solvent of toluene at 60 ^{o}C using CuCl/PMDETA catalyst system in the presence of crown initiator **11**. The conditions and results are given in Table 4.1. The plot of ln $[M]_0/[M]$ versus time for PMMA was linear indicating that the rate of polymerization is first order with respect to monomer concentration, which the concentration of radicals was constant throughout the polymerization. The experimental number avarege molecular weights of PMMA were determined by GPC based on the linear PMMA standards. The observed molecular weights of the polymers showed some deviations from those calculated by theoretical ones. The reasons of these results can be attributed to the different hydrodynamic volumes of crown ether. polydispersity values tend to decrease during the polymerization. The polymerization reactions were carried out using PMMA as macroinitiator SFRP of styrene (St) in bulk at 125 ^{0}C. The observed molecular weights of PMMA-*b*-PS copolymers determined by GPC were in good agreement with the theoretical ones as can be seen in Table 4.1.

In addition, the complexation of PMMA-*b*-PS copolymer with K^+ picrate was studied by UV spectroscopy. It was observed that K^+ picrate was transferred efficiently by block copolymer from aqueous to organic phase. However, the

preparation of supramolecular miktoarm star polymer by forming intermolecular 2:1 complexation was unsuccessful. Our studies are being focused on successful synthesis of the supramolecular miktoarm star polymer using different strategy via combination of block copolymer containing a crown ether unit with larger ring size at the focal point and well-defined ammonium end functionalized homopolymer.

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AUTOBIOGRAPHY

Özcan ALTINTAŞ was born in 1980 in Sındırgı. He attempted to the Chemistry Department of Istanbul Technical University in 1998. After graduating from ITU in 2004, accepted as a master student to Istanbul Technical University, Polymer Science and Technology Department of the Institute of Science and Technology in which he is about to graduate at the moment.